JOURNAL OF THE

INSTITUTION OF CHEMISTS

(INDIA)

For Safe
reliable method of
Family Planning

Lyndiol 2.5

Organon ORGANON (INDIA) LIMITED
Himalaya House, 38 Chowringhee Road, Calcutta-16

VOL. XL SEPTEMBER, 1968 PART V

INDUSTRIAL FABRICATORS & CONSULTING BUREAU

Registered Office: 2, BRIGHT STREET, CALCUTTA-19

For:

* Fabrication and Installation of Chemical Plants & Equipments.
* Manufacture of and Technical Know-how on diverse Industrial Chemicals.
* Regular Consultancy Service on Ceramic, Chemical, Paint, Plastic, Pesticide & Allied Industries.
* Schemes and designs.
* Any other miscellaneous problems.

Kindly Contact:

M/s. INDUSTRIAL FABRICATORS & CONSULTING BUREAU

2, BRIGHT STREET, CALCUTTA-19

Gram: DEUTERIUM

Phone: 44-7778, 4627

MEMBERS OF THE COUNCIL AND OFFICERS OF THE INSTITUTION OF CHEMISTS (INDIA)

President.

SHRI B. MAITRA, M.Sc., F.I.C., Calcutta.

Past Presidents.

K. N. BAGCHI, B.Sc., M.B., D.T.M., F.R.I.C., M.Chem.A., F.N.I., Calcutta.
U. P. BASU, D.Sc., P.R.S., F.I.C., F.N.I., Calcutta.
K. S. G. DOSS, D.Sc., F.R.I.C.., F.I.C., Karaikudi.
K. A. HAMIED, M.A., Ph.D. (Berlin), F.R.I.C., F.I.C., Bombay.
J. N. MUKHERJEE, D.Sc., F.A.S., F.N.I., Calcutta.
MATA PRASAD, D.Sc., F.R.I.C., F.I.C., F.N.I., Agra.
ATMA RAM, D.Sc., F.I.C., F.N.I., Delhi.
V. SUBRAHMANYAN, D.Sc., F.R.I.C., F.I.C., F.N.I., Mysore.
S. HUSAIN ZAHEER, M.A. (Oxon), D.Phil.Nat., F.I.C., New Delhi.

Vice-Presidents.

G. M. NABAR, Ph.D., F.R.I.C., F.T.I., F.I.C., Bombay.
B. PRASAD, D.Sc. (Lond.), F.I.C., F.N.I., Patna.
SADGOPAL, D.Sc., F.R.I.C., F.I.C., New Delhi.
M. L. SCHROFF, A.B., M.S., F.I.C., Calcutta.
N. K. SEN, D.Sc., F.R.I.C., F.I.C., F.N.I., Calcutta.

Hony. Treasurer.

R. G. CHATTERJEE, D.Sc., D.I.C. (Lond.), Calcutta.

Hony. Secretary.

R. N. CHAKRAVARTI, D.Sc., P.R.S., F.R.I.C., F.I.C., F.N.I., Calcutta.

Hony. Joint Secretary.

D. CHAKRAVARTY, Ph.D., F.R.I.C., F.I.C., A.I.W.M., Calcutta.

Hony. Assistant Secretary.

A. B. DUTTA, B.Sc., A.I.C., Calcutta.

Other Members of the Council.

N. G. BASAK, M.Sc., D.Phil., F.I.C., Jealgora.
S. C. CHAKRAVARTI, M.Sc., D.Phil., F.I.C., Calcutta.
J. N. CHATTERJEE, D.Sc., D.Phil (Oxon), F.I.C., Patna.
S. K. CHATTERJEE, Ph.D., F.I.C., Calcutta.
B. N. DUTTA, M. Sc., D.Phil., F.I.C., Calcutta.
N. K. DUTTA, D.Sc., F.R.I.C., F.I.C., Calcutta.
Y. K. HAMIED, M.A., Ph.D., F.I.C., Bombay.
B. N. MEHTA, M.Sc., A.H.B.T.I., Bhuj-Kutch.
A. R. NATARANJAN, M.B.B.S., D.E.L., M.Sc. (Lond.), D.I.C. F.R.I.C., F.I.C., Madras
M. K. ROUT, D.Sc., Ph.D., F.I.C., Cuttack.
M. L. SETH, M.Sc. (Tech.), F.I.C., New Delhi.
N. M. SHAH, M.Sc., Ph.D., F.I.C., Ahmedabad.
D. L. SHRIVASTAVA, D.Sc., F.I.C., Calcutta.
D. C. TAPADAR, M.Sc., D.Phil., F.I.C., F.R.I.C., 24-Parganas.
Secretary, Ministry of Education, Government of India, New Delhi.

Editor.

S. N. MITRA, M.Sc. (Lond.), D.I.C., F.R.I.C., F.I.C.

Associate Editors.

S. C. CHAKRAVARTI, M.Sc., D. Phil, F.I.C.
B. N. DUTTA, M.Sc., D.Phil., F.I.C.
N. K. DUTTA, D.Sc., F.R.I.C., F.I.C.

Hony. Auditors.

PAL & ROY, Chartered Accountants, Calcutta.

VITAZYME

IMPROVES APPETITE

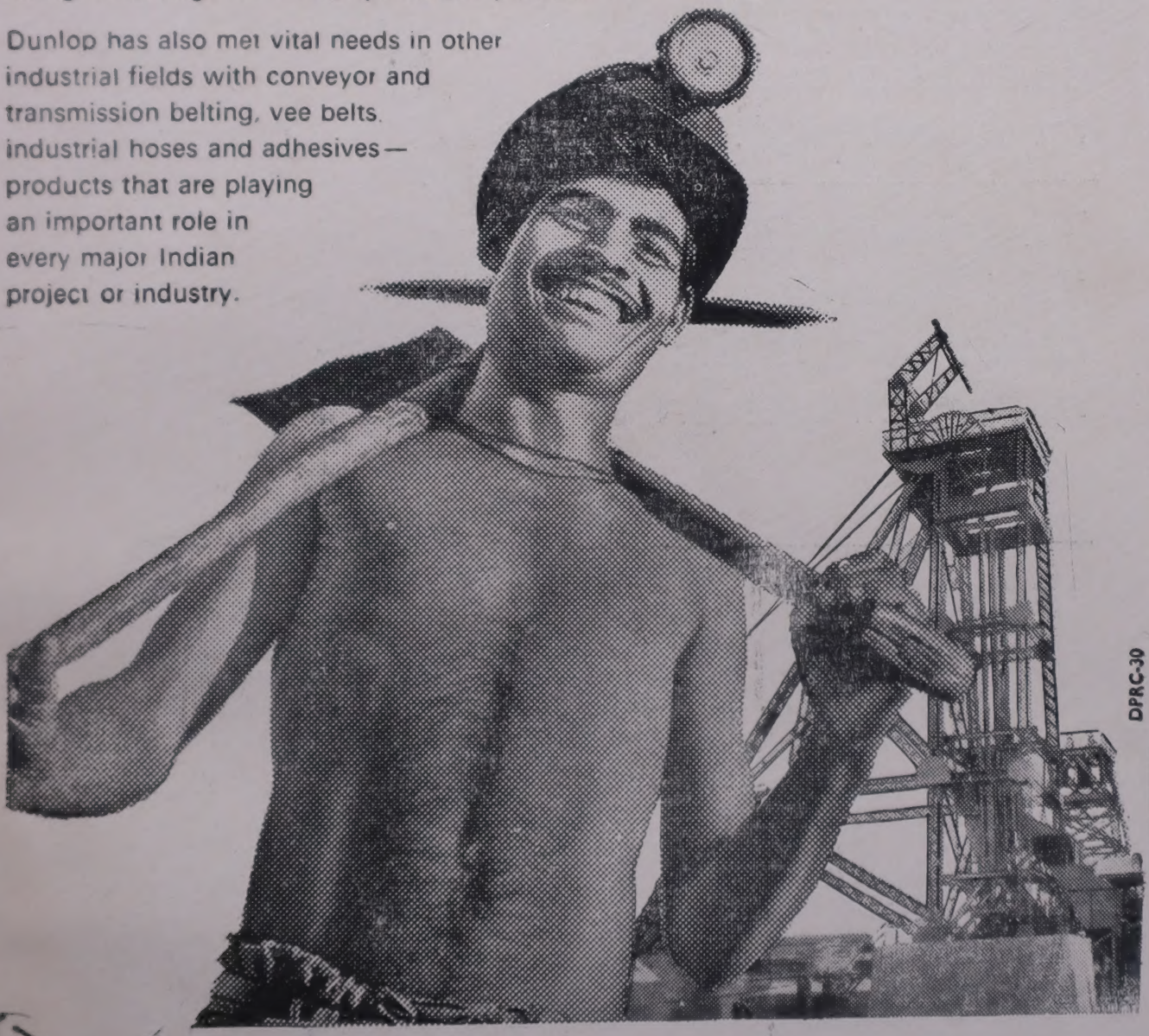
EAST INDIA PHARMACEUTICAL WORKS LTD. CALCUTTA-26

EIPW/PA/29-61

fewer fires in coal mines— Dunlop industrial products meet vital national needs

When Dunlop manufactured the first PVC fire-resistant and anti-static conveyor belting in India, they were not only helping to meet a vital need for mining safety, but also saving foreign exchange on a very specialised product

Dunlop has also met vital needs in other industrial fields with conveyor and transmission belting, vee belts, industrial hoses and adhesives— products that are playing an important role in every major Indian project or industry.



DPRC-30

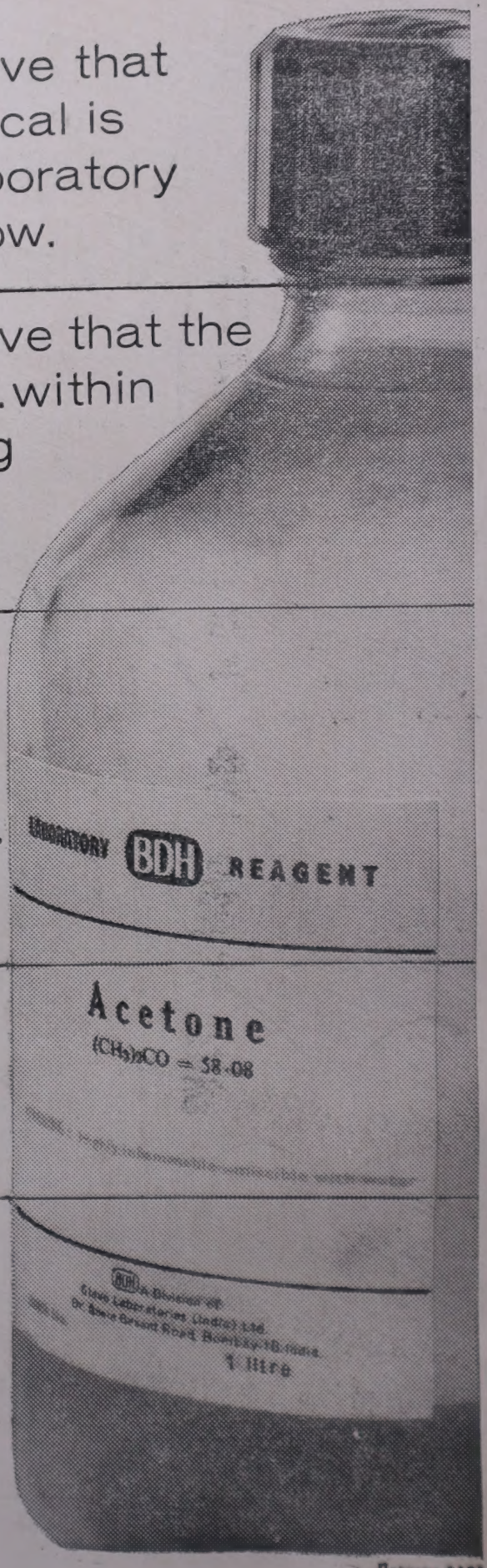
DUNLOP INDIA

—keeping pace with India's Industry

BDH does not believe that just because a chemical is used for a college laboratory its purity should be low.

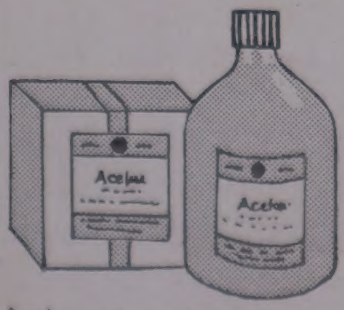
But **BDH does** believe that the price should be low...within the reach of all young scientists searching for knowledge.

That's why BDH's 'LR' range in special bulk packs is the range colleges prefer.



BDH

A Division of
Glaxo Laboratories (India) Ltd.
Dr. Annie Besant Road, Bombay-18, India.



Laboratory Reagent Bulk Packs available in 1 litre or 1 kg. packs

Bensons 0375

Telephone : 34-5585
Telegram: CHEMPROF

Institution of Chemists (India)

CHEMICAL DEPARTMENT,
MEDICAL COLLEGE,
CALCUTTA-12

26th February, 1968

NOTICE

EXAMINATION FOR THE ASSOCIATESHIP

Group A (Analytical Chemistry)

1. A.I.C. by examination is recognised as equivalent to M.Sc. degree in chemistry for purposes of recruitment of chemists as per G.O. No. F. 18—36/57-T-5, dated 19-8-58 of the Ministry of Scientific Research and Cultural Affairs. The examination with Section 2 (Drugs and Pharmaceuticals) is duly recognised in the Drugs Rules, Government of India. The nineteenth Examination is expected to be held at Calcutta in or around November, 1969, and will comprise of Theoretical, Practical and Oral tests.
2. In addition to General Chemistry (compulsory), Group A is divided into the following Sub-groups and Sections. Candidates will be required to select two subjects from amongst these (not more than one from a single Sub-Group) :

Sub-Group	*Section*	*Subject*
I	1.	Analysis of Minerals, Silicates, Ores and Alloys.
	3.	Analysis of Foods.
	9.	Analysis connected with Forensic Chemistry.
	10.	Analysis connected with Leather Chemistry.
II	2.	Analysis of Drugs and Pharmaceuticals.
	4.	Analysis of Water and Sewage.
	11.	Analysis connected with Textile Chemistry.
III	5.	Biochemical Analysis.
	6.	Analysis of Oils, Fats and Soaps.
	7.	Fuel and Gas Analysis.
	8.	Analysis of Soils and Fertilisers.

3. Number of theoretical papers is four, each of three hours' duration (Full Marks—100 in each ; Pass Marks—40% of total of theoretical). Paper I contains questions in two parts, one on organic and the other on inorganic chemistry. Paper II also contains questions in two parts, one on physical and the other on general analytical chemistry. Papers III and IV are on the two sections of applied analytical chemistry chosen by a candidate.
4. Each candidate is required to appear at practical examinations in the two sections chosen by him. The practical examination in each section continues for two days—six hours a day (Full Marks—300 in each ; Pass Marks—50% of total of practical).

5. The candidate for the 1969 examination will be required to register his name not later than 30th November, 1968, by submitting application in appropriate form and payment of a registration fee of Rs. 15/-. The candidate will also be required to submit the following with his application :—

(*i*) evidence that he has passed the B.Sc. (or its equivalent as acceptable to the Council) Examination of a recognised University *with chemistry as one of the subjects ;* (*ii*) testimonial from his employer or a gazetted officer with office seal or a Fellow of the Institution of Chemists (India) that he has, since graduation, acquired at least three years' training in the Practice of Chemistry at the time of registration ; (*iii*) two copies of his passport size photograph, one attested *with his name* at the back either by his employer or by a gazetted officer with office seal or by a Fellow of the Institution of Chemists (India), (*iv*) attested copy of a certificate of age (not below 21 years).

6. The examination fee is Rs. 85/-. The last date for submitting the fees is 31st May, 1969. Question papers of previous years are available at Rs. 2/- per year and the Syllabus at Re. 1/- per copy.

7. The candidate will be required to satisfy the examiners of his ability to translate, with the aid of dictionary, technical literatures in German, French or Russian into one of the Indian languages or English.

8. The results are published in the Proceedings of the Institution of Chemists (India). Each year Capt. N. N. Dutta Medal along with a cash prize of Rs. 200 is awarded to the best candidate.

9. Successful candidates will be admitted as Associates after payment of Rs. 12/- as admission fee and Rs. 16/- as annual subscription for the year. No admission fee, however, will be required from a candidate who is already a Member of the Institution.

10 If a candidate so desires, he may become a Member at any time prior to his passing the examination by submitting application in appropriate form and payment of Rs. 8/- as admission fee and Rs. 12/- as annual subscription, and receive the Journal and Proceedings without extra charge (usual price, Rs. 25/- per year).

11. Candidates are advised to keep in touch with issues of this Proceedings for occasional notices and announcements concerning the examination.

12. On no account should postage stamps or stamped envelopes be sent to this office. Mark sheets may be obtained at Rs. 5/- each.

13. Fees once paid will not be returned or adjusted against any other due. In all matters the decision of the Council is final.

14. All payments should be made by crossed cheque with 70 paisa extra as Bank charges or by Crossed Indian Postal Order but not by Money Order.

R. N. CHAKRAVARTI
Honorary Secretary

JOURNAL OF THE
INSTITUTION OF CHEMISTS (INDIA)

VOL. XL SEPTEMBER, 1968 PART V

CONTENTS

PAGE

1. INDEPENDENT RESEARCH 161
2. STRYCHNINE GROUP—PART—IV—*By R. N. Chakravarti* 162
3. N-α-NAPHTHYL OXAMIC ACID AS ANALYTICAL REAGENT—PART II. POTENTIOMETRIC STUDY OF COPPER (II) COMPLEXES—*By Om Prakash Gupta and J. P. Tandon* 169
4. PHYSICO-CHEMICAL STUDIES ON "PALAGUNDA" STARCH—*By M. N. Narayanan and N. Viswanadhan* 175
5. A NOTE ON PAPER CHROMATOGRAPHY OF FOOD COLOURS—*By S. N. Mitra, T. V. Mathew and P. K. Gupta* 177
6. STUDIES ON THE ION ABSORPTION CHARACTERISTICS OF Na_2O-SiO_2 GLASS DURING LEACHING IN AQUEOUS MEDIUM—*By N. K. Mitra, M. Banerjee and S. Pan* 179
7. STUDIES ON COMMERCIAL GLASS—PART III—*By H. N. Das Gupta and N. K. Mitra* 183
8. CONDUCTANCE OF TERNARY ELECTROLYTES IN DIOXANE WATER MIXTURES AT 35°C—*By P. B. Das* 191
9. INFORMATION

STEROID INTERMEDIATES

FOR RESEARCH AND INDUSTRY

CHOLESTEROL
CHOLESTEROL ACETATE
DIOSGENIN
16-DEHYDROPREGNENOLONE ACETATE
PREGNENOLONE ACETATE
PREGNENOLONE
PROGESTERONE
16L, 17L-EPOXYPREGNENOLONE
16L, 17L-EPOXYPROGESTERONE
17L-HYDROXYPROGESTERONE
17L-HYDROXYPROGESTERONE ACETATE
17L-HYDROXYPROGESTERONE HEXOATE
16-DEHYDROPREGNENOLONE ACETATE OXIME
ANDROSTENOLONE (Dehydroepiandrosterone)
ANDROSTENOLONE ACETATE
ANDROSTENEDIONE
METHYLANDROSTENEDIOL
METHYLTESTOSTERONE
TESTOSTERONE
TESTOSTERONE ACETATE
TESTOSTERONE PROPIONATE
TESTOSTERONE HEXAHYDROBENZOATE
CHOLIC ACID
DEHYDROCHOLIC ACID

THE ABOVE COMPOUNDS ARE AVAILABLE FROM:

'CIPLA'-STEROID DIVISION

289, BELLASIS ROAD, BYCULLA BOMBAY-8.

Journal of the
Institution of Chemists (India)

Vol. XL SEPTEMBER, 1968 Part V

INDEPENDENT RESEARCH

In the preindependence days, most of the Indian Universities had provision for D.Sc. only available through independent research. After independence, provision has been made for Ph.D./D.Phil. for which it is necessary to work under a guide. Independent research is mainly in the interest, if any, of the individual scientist concerned. If some work is good, it is immaterial to the country whether it is the work of one or more. In view of the great interest used to be shown to this item during selections, promotions, etc., a young scientist is sometimes tempted to find out ways and means for carrying out independent research. This tendency is often the cause of various troubles in research laboratories. On the other hand, in Western laboratories team work is the usual motto. A single scientist may do a little thing but if the cooperation of others are pulled together better work is possible and there is better chance for training others. Such a system is obviously much better in the general interest. In a University, where after M.Sc. one may try either for Ph.D. or for D.Sc., some of the Ph.D.'s are much better than post-independence D.Sc.'s as it is easier for a Ph.D. worker to be associated with better type of research and to have a much better training under a reputed guide than one who carries out independent research for his D.Sc.

Sometimes a junior complains that his senior is quite unreasonably, insisting on inclusion of his name in a paper. It is also not unusual for a senior to complain that his junior has published a joint work independently. More serious troubles may arise in the distribution of royalties. Though in such matters, normally, the opinion of the senior worker and guide should prevail, he should not have the right to exclude the proper claims for collaboration by a junior. Discipline in a laboratory is a prime need and a junior of ti-day should remember that by curtailing the rights and privileges of the senior he may not ultimately gain if he aspires to be the senior of to-morrow. A more clever fellow looks to his overall gains in the long run in all such and other matters.

R. N. C.

STRYCHNINE GROUP—PART IV*

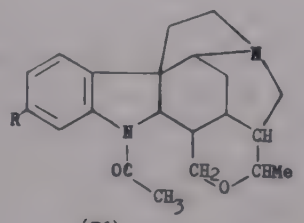
By

R. N. Chakravarti

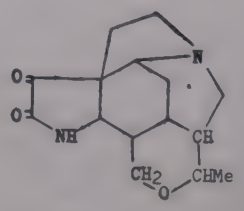
Chemistry Department, School of Tropical Medicine, Calcutta-12

Strychnospermine and Spermostrychnine

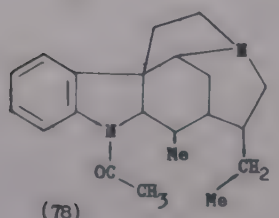
Introduction : The leaves of *Strychnos psilosperma* F. Muell., a sprawling shrub of Australia, contains total alkaloid to the extent of 1·1%, of which 0·9% is strychnospermine and 0·05% is spermostrychnine. Previously the leaves were found to contain strychnine, brucine and strychnicine, but Anet, Hughes and Ritchie[1] after examination of several samples could not confirm the presence of these alkaloids in the leaves. On the other hand, they isolated the alkaloids, strychnospermine and spermostrychnine. The structures for these two alkaloids were established by Anet and Robinson[2] as (76, R=OMe) and (76, R=H) respectively on the basis of their experimental studies.



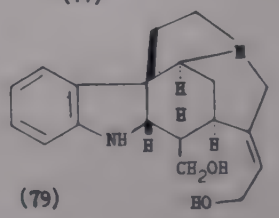
(76)



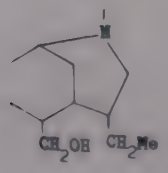
(77)



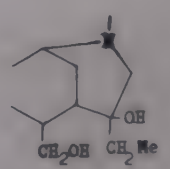
(78)



(79)



(80)



(81)

Strychnospermine : Strychnospermine, $C_{22}H_{28}O_4N_2$, crystallizes from methanol in colorless needles, m.p. 208-209°, $[\alpha]_D^{16}$ +60·3° (chloroform). It yields a hydrochloride, B.HCl, which chars at about 300° and melts with effervescence at 330-332°, a methiodide, m.p. 335° (decomp.), a monobromostrychnospermine, m.p. 245° and by alkaline or acid hydrolysis deacetylstry-

*Contributed from Part III, this Journal, 40, July, 133-140 (1968).

chnospermine, $C_{20}H_{26}O_2N_2$, m.p. 222°. The last product yields an N-nitroso-derivative, m.p. 198-199° (decomp.). Strychnospermine gives a positive Otto reaction. It has one methoxyl group but no methylenedioxy- and methylimino-groups. N(a) is neutral, being attached to .CO.CH_3, and N(b) is tert-basic (Anet, Hughes and Ritchie[3]). Anet and Robinson[2] observed the presence of two C-methyl groups (Kuhn-Roth, macro-determination). The ultraviolet spectra of strychnospermine and deacetylstrychnospermine indicate an N-acetyl-dihydroindole and a dihydroindole structure for these respectively, containing a methoxyl group in the benzene ring (cf. Raymond-Hamet[4]). The infrared spectrum of strychnospermine shows an intense band at 6·06 μ but no absorption for NH or OH. On the other hand, deacetylstrychnospermine shows absorption for NH at 3·00 μ but no absorption for :CO. Zinc dust distillation of deacetyl-strychnospermine furnishes 3-ethylindole. Reduction of strychnospermine with lithium aluminium hydride furnishes deacetyl-N-ethylstrychnospermine. The latter on demethylation with hydrobromic acid and then fusion with phthalic anhydride affords a blue rhodamine dye, the color of which is practically identical with the rhodamine dye obtained from demethylated hexahydro-7-methoxy-11, N-dimethylcarbazole but much different from that (red-purple) obtained from demethylated hexahydro-5-methoxy-11, N-dimethylcarbazole. From this it may be inferred that the methoxyl group of strychnospermine is in the position *meta* to N(a). This was confirmed from a study of the ultraviolet spectra of deacetylstrychnospermine and strychnospermine on the one hand, and 5-, 6-, 7- and 8-methoxyhexahydrocarbazoles and their acetyl derivatives on the other. The methoxyl groups of strychnospermine (76, R=OMe) and α-colubrine (44, R=H, R′=OMe) are in similar positions. The ultraviolet spectra of the two are also similar.

Anet and Robinson[2] also carried out the demethylation of strychnospermine. With boiling hydrobromic acid deacetyldemethyl strychnospermine is formed and the latter on acetylation readily furnishes demethylstrychnospermine (76, R=OH) soluble in aqueous alkali. Chromic acid oxidation of the product affords a water-soluble compound (77), $C_{15}H_{20}O_3N_2$, analogous to dioxonucidine of Leuchs and Kröhnke[5]).

Spermostrychnine : Spermostrychnine, $C_{21}H_{26}O_2N_2$, crystallizes from acetone in colorless needles, m.p. 208-209° (mixed m.p. with strychnospermine about 185°), $[\alpha]_D^{22}+88°$ (chloroform). The methiodide has m.p. 301-303°, and deacetylspermostrychnine, 196-198° (Anet, Hughes and Ritchie[3]). Spermostrychnine is demethoxystrychnospermine, as the compound (77), $C_{15}H_{20}O_3N_2$, obtained as above from demethylstrychnospermine, is also obtained by the chromic acid oxidation of spermostrychnine (Anet and Robinson[2]). Ultraviolet spectra of spermostrychnine and strychnine are very similar. Deoxydihydro-spermostrychnine, $C_{21}H_{28}ON_2$, is formed from deacetylspermostrychnine by the action of hydrogen bromide in acetic acid, followed by reduction of the product with zinc dust, and acetylation. It should be represented as (78) since it can be prepared from 'Wieland-Gumlich aldehyde' (42) by reduction to the corresponding carbinol (79) with lithium aluminium hydride or potassium borohydride, followed by hydrogenation in presence of palladium-charcoal to (80) by

hydrogenolysis of the allylic hydroxyl group or to (81) by a preliminary allylic rearrangement followed by hydrogenation, heating the product with hydrogen bromide in acetic acid, reduction with zinc dust and acetylation.

Thus there is a remarkable correspondence between the structures of, on the one hand, strychnospermine (76, R=OMe) and α-colubrine (44, R=H, R′=OMe), and, on the other between spermostrychnine (76, R=H) and strychnine (2). The stereochemical configuration of strychnospermine and spermostrychnine is indicated in (79).

Calabash-curare Alkaloids of Strychnos Sp.

Introduction : In view of the remarkable paralyzing or curare activity of South American arrow poisons, alkaloids of this group have received considerable attention. The curare poisons have been classified (Boehm[6, 7]) on the basis of the containers used, e.g. 'tubecurare' when bamboo tubes were used, 'pot-curare' when earthen pots were used, and 'calabash-curare' when calabash or gourd shells were used. Calabash-curare is much more physiologically active than the others. A number of South American plants of the genus, *Strychnos*, were used along with others for making calabash-curare. Usually an aqueous extract of the bark was used.

Although Boehm[7] isolated a strongly active amorphous product from calabash-curare and King[8] obtained an amorphous quaternary iodide, having similar activity, from *Strychnos toxifera*, Wieland and his collaborators (Wieland, Konz and Sonderhoff[9]; Wieland and Pistor[10] Wieland, Pistor and Bähr[11] ; Wieland, Bähr and Witkop[12]) were the first to isolate the crystalline calabash-curare alkaloids.* The active alkaloids are quaternary bases and hence soluble in water, a property which makes the isolation of such alkaloids rather difficult. Wieland's method consists in precipitation of the bases as reineckate salts and fractionation of these by chromatography over alumina. A better method is provided by partition chromatography on cellulose (Schmid, Kebrle and Karrer[13]; Wieland and Merz[14]). Most of the basic work on isolation was carried out by King, Wieland and Karrer, and their collaborators.

Most calabash-curare alkaloids give colorations with ceric sulfate. The curare activity is determined by the head-drop assay on rabbits and mice (King[15], Waser[16]). These alkaloids may be further classified under two heads: (A) those which move faster on paper chromatogram in the usual solvent system and have little or no physiological activity, and (B) those which move comparatively slowly on the chromatogram and are responsible for most of the activity of the curares. The group (A) alkaloids have in general a $C_{19}-C_{21}$ skeleton with a basic nitrogen, N(b), and a neutral or very weakly basic nitrogen, N(a). The group (B) alkaloids, on the other hand, have double formulas with $C_{38}-C_{40}$ skeleton, two basic nitrogens, N(b), and two N(a) (von Philips-

* The chlorides of these alkaloids are usually used for most purposes and the name of the alkaloid usually signifies the chloride of the alkaloid. Thus toxiferine I means the corresponding chloride.

born, Schmid and Karrer[17]). Active calabash-curare alkaloids contain two quaternary centres.

Toxiferine I, C-Dihydrotoxiferine I, the Caracurines, and Diaboline : Toxiferine I, a strongly active quaternary alkaloid, was isolated by Wieland, Bähr and Witkop[12] from *S. toxifera* of British Guiana and C-dihydrotoxiferine I from calabash-curare of Venezuela. From a similar preparation Schmid and Karrer[18] obtained C-toxiferine I*. C-Dihydrotoxiferine I, $C_{40}H_{46}N_4^{++}$, has two N-methyl groups attached to the two quaternary nitrogen atoms, N(b). On ozonolysis it yields acetaldehyde. On dehydrogenation with sulphur it yields isoquinoline (Wieland, Witkop and Bähr[19]) and on distillation with zinc dust it yields 3-methyl- and 3-ethyl-indole (Asmis, Waser, Schmid and Karrer[20]). Nine tertiary alkaloids, caracurine I-IX, were isolated from *S. toxifera* bark of Venezuela (Asmis, Schmid and Karrer[21]). The most important discovery in this respect was made by Bernauer, Pavanaram, von Philipsborn, Schmid and Karrer[22] when it was observed that caracurine VII and Wieland-Gumlich aldehyde (43) are identical. Diaboline, a tertiary base, isolated from the bark of *Strychnos diaboli* (King[15]) is N(a)-acetyl-Wieland-Gumlich aldehyde since deacetyldiaboline is identical with Wieland-Gumlich aldehyde (43) (Battersby and Hodson[23]. Cf. Bader, Schlittler and Schwarz[24]).

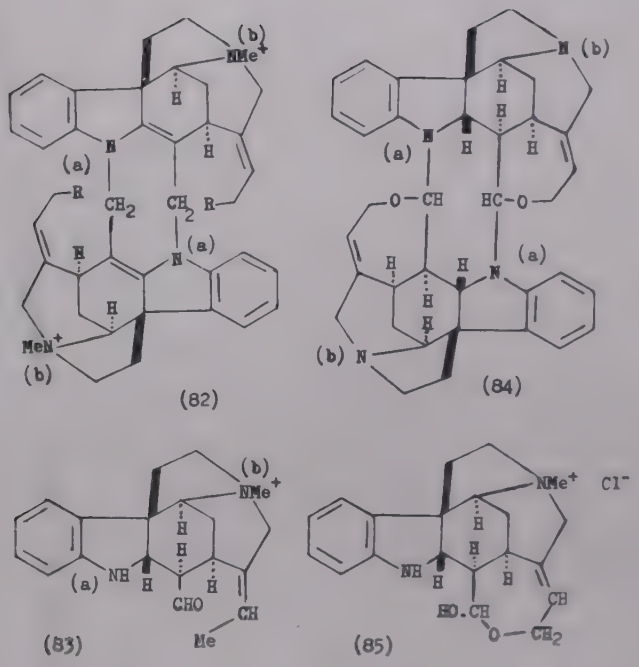
Two extremely interesting changes were observed by Karrer, Schmid and their collaborators (Bernauer, Schmid and Karrer[25]; Bernauer, Berlage, von Philipsborn, Schmid and Karrer[26]). The C_{40}— alkaloid, C-dihydrotoxiferine I (82, R=H) is converted by mineral acid into the C_{20} -alkaloid, hemidihydrotoxiferine (83). Moreover, the latter can be reconverted into the former in presence of dilute acetic acid and sodium acetate (pH 5). Taking advantage of this bimerization reaction caracurine V (84) was synthesized from Wieland-Gumlich aldehyde (43). Caracurine V (84) can be converted into Wieland-Gumlich aldehyde (43) by dilute mineral acid. Following more or less the same track, Wieland-Gumlich aldehyde methochoride (85) can be converted into toxiferine I(82, R=OH) and *vice versa* (Berlage, Bernauer, von Philipsborn, Waser, Schmid and Karrer[27] Battersby and Hodson[28, 29])*.

C-Fluorocurarine (C-Curarine III) and C-Curarine I : The yellow quaternary alkaloid, C-fluorocurarine, was isolated by Wieland, Pistor and Bähr[11] from calabash-curare and detected in the bark of *Strychnos mitscherlischii* Rich. Schomb. (Kebrle, Schmid, Waser, and Karrer[30]). It has one N-methyl group attached to N(b) and one C-methyl group in an ethylidene side chain. Formation of N(a)-acetylfluorocurarine indicates presence of :N(a)H. C-Fluorocurarine has an absorption peak at 358 mμ which in presence of alkali shows a bathochromic shift (reversible). N(a)-methyl-C-fluorocurarine has identical absorption peak but does not show the bathochromic shift which appears to be due to absence of a removable proton at N(a) in the latter. From a critical study of the borohydride reduction products of this N(a)-methyl derivative von

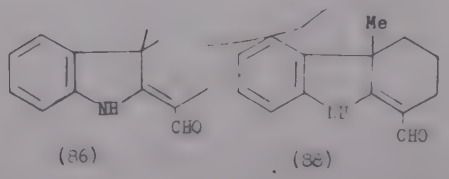
---

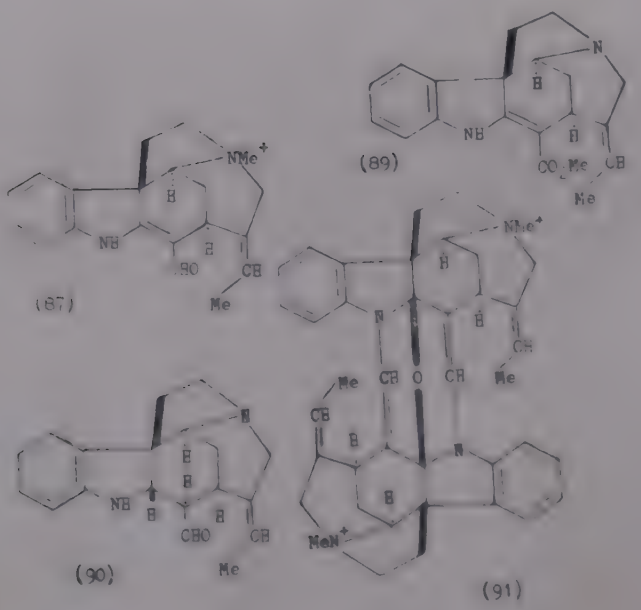
* 'C'—indicates that the source is calabash-curare. Toxiferine I and C-toxiferine I are accepted as identical.

* C-Dihydrotoxiferine I is really a desoxytoxiferine I.



Philipsborn, Meyer, Schmid and Karrer[31] concluded that the chromophoric system as in (86) is present in the parent alkaloid, the latter being represented as (87). In line with this, the parent alkaloid has infrared absorption bands similar to those of $\alpha:\beta$-unsaturated- β -amino-aldehydes This was confirmed by Fritz (1959) by preparation of the model aldehyde (88), which has similar absorption peak in neutral and alkaline media as C-fluorocurarine. There





is a remarkable similarity between structure (87) for fluorocurarine and that of akuammicine (89) (Aghoramurthy and Robinson[32]). The structure (87) was confirmed by Fritz, Besch and Wieland[33]. (Cf. von Philipsborn, Meyer, Schmid and Karrer[31]) by hydrogenolysis of the allylic OH of the Wieland-Gumlich glycol (79), Oppenauer oxidation to the corresponding aldehyde, norhemidihydrotoxiferine (90) followed by an oxidation and methylation at N(b) to C-fluorocurarine (87). C-curarine I, which furnishes C-fluorocurarine by the action of concentrated hydrochloric acid (Zürcher, Ceder and Boekelheide[34]; Fritz and Wieland[35]), has been formulated as (91) by Karrer, Schmid and their collaborators (Nagyvàry, Arnold, von Philipsborn, Schmid and Karrer[36]).

Other Alkaloids of Strychnos SP.

A number of other alkaloids have been isolated from other strychnos plants e.g. *S. henningsii* Gilg. of South Africa, *S. icaja* of Congo, *S. angolensis*, *S. holstii*. From the last one four alkaloids, holstiine, holstiline, condensamine and retuline, have been isolated by chromatography (Bosly[37]). *Strychnos melinoniana* Bail, yields a number of alkaloids (Schlittler and Hohl[38]; Bächli, Vamvacas, Schmid and Karrer[39]) but these contain the β-carboline ring system.

References

1. F. A. L. Anet, G. K. Hughes and E. Ritchie, Nature, *166*, 476 (1950).
2. F. A. L. Anet and R. Robinson, J. Chem. Soc., 2253-2262 (1955).
3. F. A. L. Anet, G. K. Hughes and E. Ritchie, Australian J. Chem., *6*, 58-65 (1953).
4. Raymond-Hamet, Ann. pharm. franc., *8*, 482-490 (1950).
5. H. Leuchs and F. Kröhnke, Ber., *63*, 1045-1056 (1930).
6. R. Boehm, Abh. kgl. Sächs. Ges. Wiss., *22*, 201-238 (1895).
7. R. Boehm, Abh. kgl. Sächs. Ges. Wiss., *24*, 1-52 (1897).
8. H. King, Nature, *135*, 469-470 (1935).
9. H. Wieland, W. Konz and R. Sonderhoff, Ann., *527*, 160-168 (1937).
10. H. Wieland and H. J. Pistor, Ann., *536*, 68-77 (1938).
11. H. Wieland, H. J. Pistor and K. Bähr, Ann., *547*, 140-155 (1941).
12. H. Wieland, K. Bähr and B. Witkop, Ann., *547*, 156-179 (1941).
13. H. Schmid, J. Kebrle and P. Karrer, Helv. Chim. Acta, *35*, 1864-1879 (1952).
14. T. Wieland and H. Merz, Chem. Ber., *85*, 731-743 (1952).
15. H. King, J. Chem. Soc., 955-958; 3263-3271 (1949).
16. P. Waser, Helv. Physiol. Pharmacol. Acta, *8*, 342-350 (1950).
17. W. von Philipsborn, H. Schmid and P. Karrer, Helv. Chim. Acta, *39*, 913-922 (1956).
18. H. Schmid and P. Karrer, Helv. Chim. Acta, *30*, 1162-1171 (1947).
19. H. Wieland, B. Witkop and K. Bähr, Ann., *558*, 144-156 (1947).
20. H. Asmis, P. Waser, H. Schmid and P. Karrer, Helv. Chim. Acta, *38*, 1661-1668 (1955).
21. H. Asmis, H. Schmid and P. Karrer, Helv. Chim. Acta, *37*, 1983-1992 (1954).
22. K. Bernauer, S. K. Pavanaram, W. von Philipsborn, H. Schmid and P. Karrer, Helv. Chim. Acta, *41*, 1405-1407 (1958).
23. A. R. Battersby and H. F. Hodson, Proc. Chem. Soc., 126 (1959).
24. F. E. Bader, E. Schlittler and H. Schwarz, Helv. Chim. Acta, *36*, 1256-1266 (1953).
25. K. Bernauer, H. Schmid and P. Karrer, Helv. Chim. Acta *41*, 1408-1410 (1958).
26. K. Bernauer, F. Berlage, W. von Philipsborn, H. Schmid and P. Karrer, Helv. Chim. Acta, *41*, 2293-2308 (1958).
27. F. Berlage, K. Bernauer, W. von philipsborn, P. Waser, H. Schmid and P. Karrer, Helv. Chim. Acta, *42*, 394-397 (1959).
28. A. R. Battersby and H. F. Hodson, Proc. Chem. Soc., 287-288 (1958).
29. A. R. Battersby and H. F. Hodson, J. Chem. Soc., 736-741 (1960).
30. J. Kebrle, H. Schmid, P. Waser and P. Karrer, Helv. Chim. Acta, *36*, 345-349 (1953).
31. W. von Philipsborn, H. Meyer, H. Schmid and P. Karrer, Helv. Chim. Acta, *41*, 1257-1273 (1958).
32. K. Aghoramurthy and R. Robinson, Tetrahedron, *1*, 172-173 (1957).

33. H. Fritz, E. Besch and T. Wieland, Angew. Chem., *71,* 126 (1959).
34. A. Zürcher, O. Ceder and V. Boekelheide, J. Am. Chem. Soc., *80,* 1500-1504 (1958).
35. H. Fritz and T. Wieland, Ann., *611,* 277-279 (1958).
36. J. Nagyvàry, W. Arnold, W. von Philipsborn, H. Schmid and P. Karrer, Tetrahedron, *14,* 138-149 (1961).
37. J. Bosly, J. pharm. Belg., *6,* 150-177, 243-266 (1951).
38. E. Schlittler and J. Hohl, Helv. Chim. Acta, *35,* 29-45 (1952).
39. E. Bächli, C. Vamvacas, H. Schmid and P. Karrer, Helv. Chim. Acta, *40,* 1167-1187 (1957).

J. Inst. Chemists (India), Vol. XL, September, 1968

N-α-NAPHTHYL OXAMIC ACID AS ANALYTICAL REAGENT PART II. POTENTIOMETRIC STUDY OF COPPER (II) COMPLEXES

By

OM PRAKASH GUPTA & J. P. TANDON

Chemical Laboratories, B. R. College, Agra & University of Rajasthan, Jaipur.

(Received for publication on 25-1-68).

Copper, being almost the last member of the first transition series, depicts a strong tendency of complex formation. In an earlier communication[1], it has been reported that copper (II) forms 1 : 2 chelate with N-α-naphthyl oxamic acid[2] and the reagent has been found suitable for its macro as well as semi-micro determinations. In the present studies, the formation of 1 : 1 and 1 : 2 derivatives has been shown potentiometrically ; it is further supported by preparative studies. The 1 : 1 derivative is formed at higher pH>5. Fod comparison, studies with N-α-naphthyl malonamic acid[3] have also been carried out.

EXPERIMENTAL

Solution of copper nitrate, $Cu(No_3)_2.3H_2O$, was prepared by using E. Merck G. R. product and standardised iodometrically. Potassium hydroxide and acetic acid solutions of suitable strength were prepared from A. R. grade samples. An alcoholic solution of N-α-naphthyl oxamic acid was prepared by dissolving the pure compound in 80% alcohol. Potassium salt solutions of N-α-naphthyl oxamic acid(I) and N-α-naphthyl malonamic acid (II) were prepared by dissolving known weights in standard potassium hydroxide solution.

pH measurements were carried out at room temperature with a Cambridge Bench type pH meter, standardised against 0·05M potassium hydrogen phthalate solution. Each titration was repeated at least twice and the reproducibility was established. All the solutions for pH measurements were made in conductivity water.

The pH measurements of the following systems were carried out :

(1) 100 ml of an aqueous solution of N-α-naphthyl oxamic acid (0·004M) against 0·04M KOH (Fig. 1).

(2) 10 ml of 0·04M copper nitrate against 0·04M reagent (I) (Fig. 2, curve A).

(3) 10 ml of 0.04M copper nitrate (pH lowered to 2·5) against 0·04M reagent(I) (Fig. 2, curve B).

(4) 10 ml of 0·04M copper nitrate against 0·04M reagent (II) (Fig. 2, curve C).

(5) 20 ml of 0·04M copper nitrate+20 ml of 0·04M reagent(I), against 0·5M KOH (Fig. 3, curve A).

(6) 20 ml of 0·04M copper nitrate+40 ml of 0·04M reagent (I), against 0·5M KOH (Fig. 3, curve B).

(7) 20 ml of 0·04M copper nitrate+60 ml of 0·04M reagent (I), against 0·5M KOH (Fig. 3, curve C).

(8) 20 ml of 0·04M copper nitrate against 0·5M KOH (Fig. 3, curve D).

(9) 5 ml of 0·04M copper nitrate+20 ml of 0·02M alcoholic solution of N-α-naphthyl oxamic acid+35 ml of 0·04M KOH, against 0·04M acetic acid (Fig. 4, curve A).

(10) 5 ml of 0·04M copper nitrate+10 ml 0·04M reagent(I)+20 ml of 0·04M KOH, against 0·01M acetic acid (Fig. 4, curve B).

Results and Discussion

System (I)

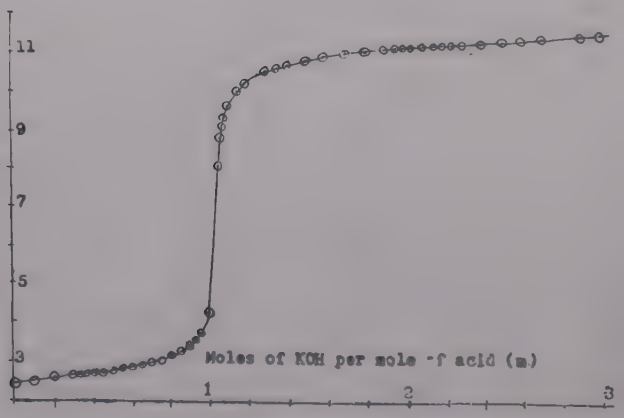
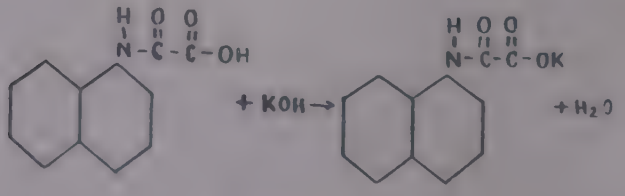


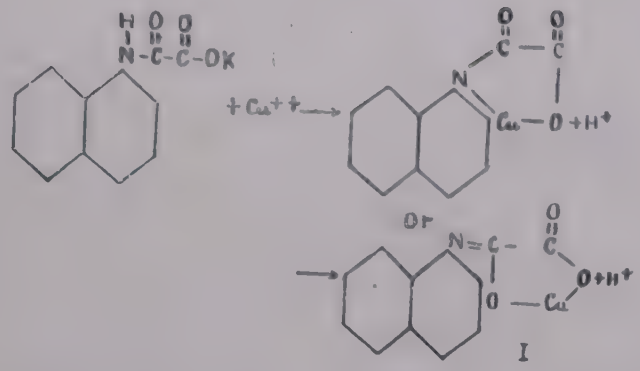
Fig. 1

The curve in Fig. 1 shows only one inflection point at m=1. It indicates the neutralisation of hydrogen of the carboxyl group, while that of the imino group is not titrable.



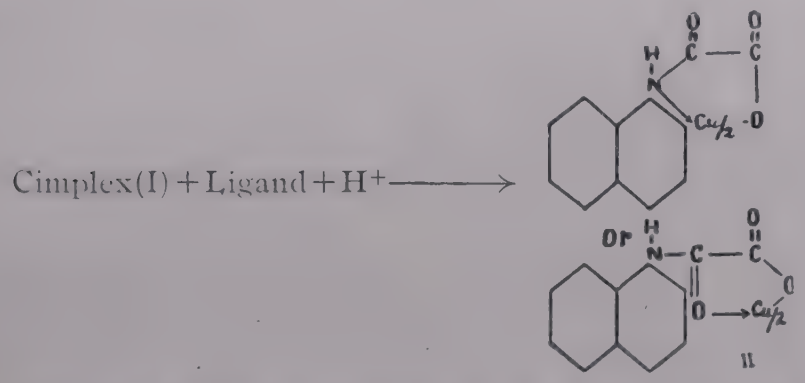
System (II)

Curve A, Fig. 2 shows an inflection point at m=2. On the addition of reagent(I) to copper nitrate, the pH is lowered. This initial fall may be due to the liberation of hydrogen ions on the formation of 1:1 complex as given below:



I

The complex(I) being unstable at low pH, soon rearranges to 1 : 2 derivative as a result of which the pH rises again. The conversion may take place as follows :



II

This sort of behaviour continues on each addition of the reagent. However, in the beginning this change appears to be slow.

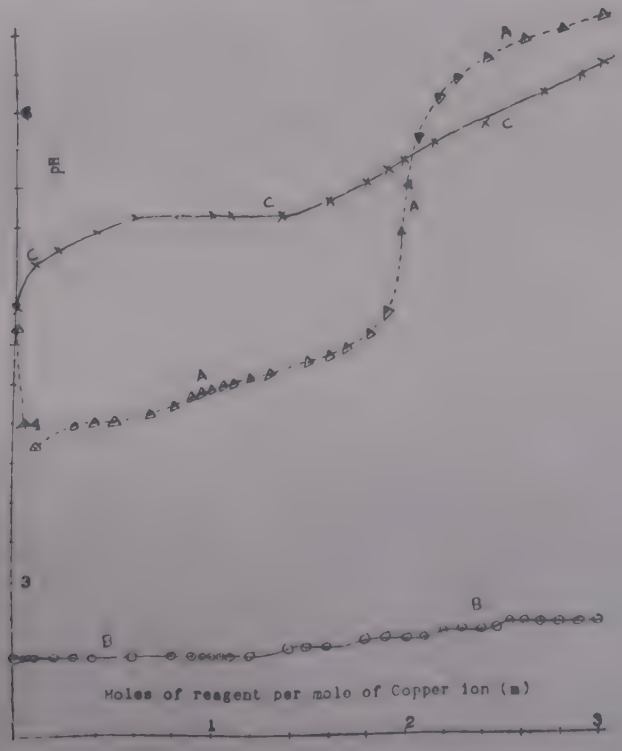


FIG. 2

Curve B, Fig. 2, shows that at pH 2·5, the hydrogen of the imino group is not liberated and only 1 : 2 complex (II) is formed. Curve C, Fig. 2, is the plot of copper nitrate titrated against reagent (II), i.e., the potassium salt of N-α-naphthyl malonamic acid. In this case there is no lowering of pH and no well defined inflection at m=2. The greenish white precipitate obtained is somewhat soluble in water and is decomposed by sodium hydroxide, giving the precipitate of copper hydroxide. It also dissolves in ammonium hydroxide giving deep blue colour. On the other hand, the greenish white precipitate of copper(II) with N-α-naphthyl oxamic acid is insoluble even in hot water and dissolves in sodium and ammonium hydroxides giving deep green solutions. This deep green colour persists even on the addition of tartrate. The precipitate is also soluble in pyridine giving again a deep green coloured solution. The stability of the copper compound of N-α-naphthyl oxamic acid may be due to the fact that in this reagent the salt forming carboxyl group and coordinating imino or carbonyl group are so located so as to favour the formation of five-membered ring, whereas in N-α-naphthyl malonamic acid the less stable six-membered ring is formed and hence the copper compound is less stable.

System (III)

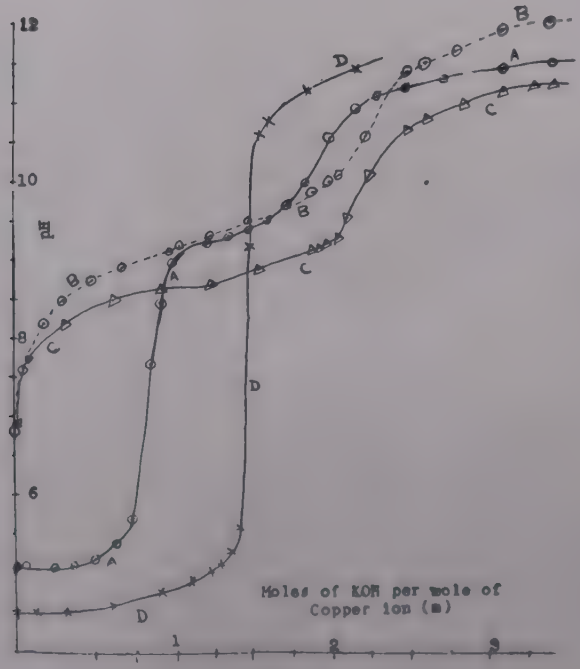
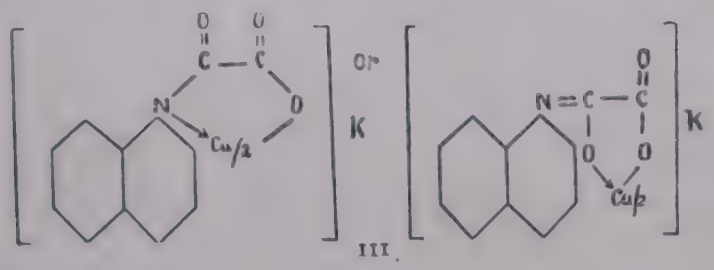


FIG. 3

Curves B and C, Fig. 3, indicate inflection points at about m=2. During successive additions of potassium hydroxide the precipitate dissolves, the process of dissolution being slow, hence vigorous shaking was done before the reading was recorded. The dissolution may be due to the loosening of hydrogen of the imino group, which becomes more mobile after chelation. However, in the present it is not so as is evident from Fig. 1.

The dissolution may be represented as follows:



III.

The resulting deep green solution remains clear for several hours, but on long standing a reddish brown compound separated and a whitish deposit of the potassium salt of N-α-naphthyl oxamic acid was observed along the sides of the vessel.

Curve D, Fig. 3, is very much similar to the one given by Britton[4] and shows inflection point at m=1·5. However, curve A, Fig. 3 shows two inflection points, first at m=0·75 and the second at m=1·75. In this case, the metal to ligand ratio is 1 : 1 ; hence only half of the copper is precipitated as 1 : 2 complex, while the other half remains free. The first point of ;nflection in curve A corresponds to the precipitation of free copper as copper hydroxide, while the second point depicts the dissolution of the chelated copper. At the end of the titration the light blue precipitate of copper hydroxide settled down in the deep green solution.

Curve A, Fig. 4, shows the inflection point at m=3, indicating that out of seven moles of potassium hydroxide added, four moles are consumed by the system—two by the carboxyl groups and two by the hydrogens of the imino groups.

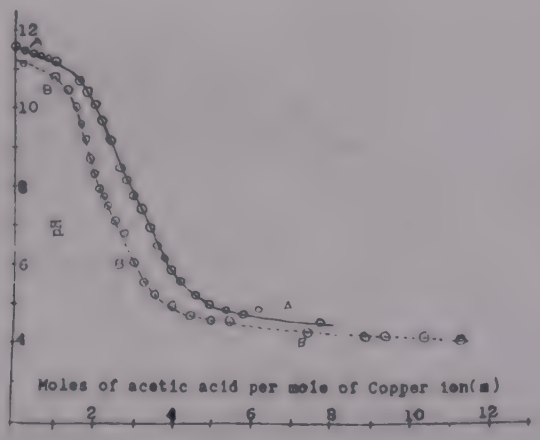


FIG. 4

Curve B, Fig. 4, indicates the inflection point at m=2 showing that out of four moles of alkali added only two are consumed by the system, i.e., by two hydrogens of imino groups in 1 : 2 complex.

Preparative Studies :

The results obtained by the potentiometric studies have been confirmed further by isolating and analysing the complexes.

1 : 2 Complex :

An aliquot of the standard copper nitrate solution was taken and 1% solution of the potassium salt of N-α-naphthyl oxamic acid was added so that copper to ligand ratio was 1 : 2 (pH, 6·2). A dirty green precipitate was obtained, which soon changed to greenish white colour. It was filtered, washed with hot water and finally with alcohol. The precipitate was dried at 100° C and analysed. The analysis corresponds to $(C_{10}H_7NH\ CO\ COO)_2Cu$.

Found : Cu, 12·90 ; N, 5·67% ; Calc. for $(C_{10}H_7NHCOCOO)_2Cu$, Cu, 12·91; N, 5·69%.

1 : 1 Complex :

An aliquot of the standard copper nitrate solution was taken and the pH was raised to about 5·0 with potassium hydroxide. The ligand(I) was then added so that metal to ligand ratio was I : 1. A yellowish-brown precipitate was obtained, which when kept for about three hours changed to reddish brown colour. It was filtered, washed and dried as above. The analysis corresponds to $(C_{10}H_7N.CO.COO)Cu$.

Found : Cu, 22·90 ; N, 4·88% ; Calc. for $(C_{10}N_7N.CO.COO)Cu$; Cu, 22·96 ; N, 4·90%.

The reddish brown compound obtained during the potentiometric study of system(III) was found to be identical to the above product.

The greenish white copper compound with N-α-naphthyl malonamic acid was also prepared the same way. It was analysed and the analysis corresponds to $(C_{10}H_7NH.CO.CH_2.COO)_2Cu$.

Summary

The complexation reactions of copper (II) with N-α-naphthyl oxamic acid have been investigated by potentiometry and the correctness of the assumed formation of 1 : 1 and 1 : 2 complexes has been further confirmed by preparative studies. For comparison, a preliminary study with N-α-naphthyl malonamic acid has also been carried out.

Acknowledgement

The authors are grateful to Prof. R. C. Mehrotra, Head of the Chemistry Department, University of Rajasthan, Jaipur and the authorities, B. R. College, Agra for encouragement and providing laboratory facilities.

References

1. Om Prakash Gupta and J. P. Tandon, Indian J. Chem., (In Press).
2. M. Busch, *Ber.*, *6*, 240 (1873).
3. R. C. Agarwal and P. L. Trivedi, Agra Univ. J. Res. Sci., *13*, 52 (1964).
4. H. T. S. Britton, "Hydrogen Ions", Chapman and Hall, London, 4th Ed., *2*, 88 (1956).

J. Inst. Chemists (India), Vol. XL, September, 1968

PHYSICO-CHEMICAL STUDIES ON "PALAGUNDA" STARCH

By

M. N. Narayanan and N. Viswanadham

Department of Pharmacy, Andhra University, Waltair.

(Received for publication on 13-2-68)

Starch, besides constituting an important item of our food, serves as a raw material in a large number of industries and the increasing requirements of starch have necessitated the tapping of new sources of commercial starches. The properties of starches vary to some extent, depending upon the vegetable sources from which they are derived, some being more suitable for particular industries than others.

"Palagunda" (Genus: *Curcuma*) is a farinaceous material produced on a cottage industry scale by the hill tribes of Visakhapatnam and Srikakulam districts in Andhra Pradesh and the neighbouring hill tracts of Orissa state. It is reputed to be easily digestible and is used for making milk puddings and as a diet for children and invalids. The preparation of "Palagunda" from the wild tubers and its commerce have been described by Somayajulu,[1] but adequate information concerning its properties is not available in the literature. Hence, we have taken up a detailed examination of "Palagunda" starch for its physical and chemical properties. The present work forms a part of our investigations of the various native Indian starches.

Experimental

Starch samples : Five samples of Palagunda starch were obtained from the local Visakhapatnam market. They were in the form of small irregular hard masses, varying in colour from white to pale yellow. All samples had the characteristic aromatic odour usually associated with the genuine material. They were powdered and kept in air-tight bottles for further examination.

Microscopic appearance : The starch was made into a thin suspension with water and a drop was examined under the microscope fitted with a calibrated micrometer eye-piece. The size of the granules varied between 9 to 120 microns in length and 6 to 40 microns in breadth. They appeared to be ovoid to ellipsoid in shape with faint striations and with a well marked cross under polarised light.

Analysis : Moisture was determined by the toluene distillation method.[2] The starch content was determined by direct acid hydrolysis followed by the estimation of dextrose by Lane and Eynon's volumetric method. Petrol-soluble substances were estimated by continuous extraction with petroleum ether (b.p. 40-60°) in a Soxhlet apparatus. Total ash, water-soluble ash and acid-insoluble

ash were found by the method recommended by Woodman.[3] The phosphorus content was determined by the AOAC method for the estimation of phosphorus in wheat flour.[4] The analytical data are given in the following table.

TABLE I

Composition of Palagunda Starch

Sample No.	Moisture %	Starch %	Petrol soluble substances %	Ash			Phosphorus (as P_2O_5) %
				Total %	Water-soluble %	Acid-insoluble %	
I	18·00	78·03	0·25	1·43	0·30	0·73	0·252
II	16·80	80·21	0·18	1·10	0·17	0·50	0·207
III	18·40	78·07	0·19	1·10	0·23	0·45	0·222
IV	17·20	81·36	0·12	0·87	0·25	0·40	0·186
V	17·40	80·72	0·15	0·95	0·30	0·37	0·192

Discussion

The proximate analysis of "Palagunda" starch shows that the material as available in the market is of good quality and consists of almost pure starch (about 96·65% when calculated on moisture-free basis). Preliminary experiments showed that "Palagunda" starch gives solutions of high viscosity even at very low concentrations. In this respect and also in microscopic appearance "Palagunda" starch closely resembles arrowroot starch. Further work on gelatinisation properties, viscosity of starch pastes, fractionation of the starch etc. is in progress and results will be communicated later.

Summary

Microscopic examination and proximate analysis, including moisture, starch content, petrol-soluble substances, ash and phosphorus content of "Palagunda" starch obtained from the Visakhapatnam market are described. Its close resemblance to arrowroot starch is also noted.

References

1. P. Somayajulu, The Madras Agricultural Journal, 27, 442 (1939).
2. A. G. Woodman, Food Analysis, McGraw Hill Book Co., New York, p. 21 (1941).
3. *Ibid*., p. 23.
4. Official Methods of Analysis of the AOAC, published by the Association of Official Agricultural Chemists, Washington D. C., p. 160 (1960).

J. Inst. Chemists (India), Vol. XL, September, 1968

A NOTE ON PAPER CHROMATOGRAPHY OF FOOD COLOURS

By

S. N. Mitra, T. V. Mathew and P. K. Gupta

Central Food Laboratory, Calcutta.

(*Received for publication 6-2-68*)

For the detection and identification of coaltar colours added to foods Spot test with the dyed wool is not always reliable, and moreover, mixtures of colours cannot be separated and identified by this test. Chromatography is a convenient method of separating and identifying the colours. For such identification, it is necessary to determine the chromatographic patterns of standard permitted coal tar food colours (which are all acidic water soluble colours). Eleven common permitted food colours have been studied for their chromatographic behaviour and the observations are recorded here. Also, an unknown sample of syrup was tested for the colour present.

Paper Chromatography—Whatman No. 1 filter paper was used throughout cut into strip of the size 40×10 c.m. The standard permitted colours which were tested are—Ponceau 4R, erythrosine, indigo-carmine, carmoisine, tartrazine, Sunset yellow, Fast Red E, Red FB, Red 6B, Acid magenta and Amarnath. Two solvents were used, namely, (a) iso-amyl alcohol : 95% ethanol : $NH_4OH : H_2O$ (4 : 4 : 1 : 2) and (b) 2% sodium citrate in 5% NH_4OH. It was observed that solvent (a) is specially suitable for red colours. The concentration of the aqueous colour solution was 0·01% and the spotting was done in the usual manner by a capillary tube. By descending chromatography the following result was obtained (Table 1).

Results

The above table is useful in identifying unknown colours in articles of food. For example—A sample of Syrup was extracted by wool in the usual way and the colour extracted from the dyed wool was spotted on No. 1 whatman paper, and the chromatogram was run in the descending type for 3 hours in solvent B. The Rf value of the red spot was 0·06 indicating that the colour may be Fast Red E, Red 6B or carmoisine.

The chromatograph was repeated in solvent A with 18 hrs. run. Rf value of the spot was 0·1 indicating that the colour was carmoisine. This was further confirmed by spotting the test dye solution and carmoisine side

by side in the same paper and running in solvent A. Rf values of both the spots were 0·1.

Further work with other colours and different solvents is in progress.

TABLE I

Rf values of Food colours using two solvents

Name of the colour	Rf values	
	Solvent A	Solvent B
Red		
Ponceau 4R	0·183	0·437
Erythrosine	0·560	0·018
Carmoisine	0·10	0·085
Fast Red E	0·09	0·07
Amaranth	0·05	0·15
Red 6B	—	0·056
Red FB	—	0·0
Acid Magenta	—	0·89
Yellow		
Tartrazine	—	0·471
Sunset Yellow	—	0·21
Blue		
Indigo-Carmine	0·113	—

Solvent A—Iso-amyl alcohol : 95% ethanol : NH_4OH : H_2O (4 : 4 : 1 : 2). 18 hours run in descending type. Solvent front was 24·6 c.m.

Solvent B—2% Sodium citrate in 5% NH_4OH. 3 hours run in descending type. Solvent front was 17·8 c.m.

J. Inst. Chemists (India), Vol. XL, September, 1968

STUDIES ON THE ION ABSORPTION CHARACTERISTICS OF Na_2O-SiO_2 GLASSES DURING LEACHING IN AQUEOUS MEDIUM

By

N. K. Mitra, M. Banerjee and S. Pan

Department of Applied Chemistry
Calcutta University.

(*Received for publication on 20-1-68.*)

From physical appearance glasses appear to be very rigid but the same is not true when they are in contact with aqueous phase and some of the glass forming constituents loose their stability from the mother structure depending on the composition of the glass as well as the solution. The subject of interaction of glass in the aqueous solution is being studied for a long time. In case of the soda-silica glass system silica is the network former, each silicon being tetrahedrally surrounded by the four oxygens and the alkali oxides are the network modifier and they actually modify the physical and chemical properties because they fit into the lattice holes created in the basic structure. The important property of glass, i.e. its chemical durability for which its use has been limited in some cases, is directly related to the migration of the diffusible ions from the structure.

The interaction between glass and aqueous phase during chemical corrosion cannot be fully explained on the solubility basis. According to G. W. Morey[1] the decomposition action involves mainly the penetrations of the corroding agent into the glass structure and simultaneous decomposition of the complex silicate mixture. As the physico-chemical properties of the resulting decomposition product is completely different from the original glass, it will seggregate out of the solid phase into the bulk liquid phase. The mechanism according to F. R. Von, Bichowsky[2] is that this type of interaction is first initiated by adsorption on the surface and the migration of the ions actually proceeds through this water film. Hamiltin and Hubbard[3] suggested that this is mainly an ion exchange type of reaction ixn which sodium ions are replaced by H_3O^+ ions. Douglas and Isard[4] in their work with soda-lime-silica glasses had shown that if the alkali ions are removed from the glass by an ion exchange process, the reaction rate could be controlled by the diffusion of alkali ions through the glass itself to the reaction zone. But later on it was shown[5] that the diffusion process is not simply one of the alkali ions diffusing through the glass but through the siliceous layer formed on the glass surface. This actually acts as a diffusion barrier for the ion exchange reaction in which alkalies from the glass are exchanged for other cations available in aqueous phase.

Recently Douglas[6] has concluded from his detailed work on the kineties of reactions of various binary alkali-silica glasses as well as some ternary glasses derived from them by the substitution of an alkaline earth oxide that the diffusion through the leached layer is only an important contributory factor in leaching process. Earlier explanation by the diffusion coefficient although valid for a most durable glass where the coefficient in the surface layer was not very different from that in the glass but when applied to simple binary glasses large deviation was observed. Present investigation consists in the study of the composition effect of Na_2O-SiO_2 glasses on the adsorption of cations of different valencies from the aqueous phase on the alkali deficient surface layer formed during leaching.

Experimental

The first step consists in the preparation of the glasses. The raw materials taken for this purpose were Sodium Carbonate (E. Merck) and Silica. The Silica was purified first by digestion with 6N HCl and then washed with hot water, filtered and washed free of chloride. The washed silica was finally dried at 110°C and analysed for its silica content which was found to be 99·5%. Then the purified silica was mixed with sodium carbonate in different proportions and milled in pot mill for thorough mixing. Sticks were prepared out of these mixtures in plastic conditions using dextrin as binder and dried at 110°C. The dried sticks were melted in oxyacetylene flame and the molten glass was immediately quenched in a large bulk of water. The glass particles as separated from the bulk water and again ground and melted under the same condition as stated above. The second operation was performed in order to achieve complete vitrification. Glasses were ground to −50 +80 mesh followed by thorough washing with acetone and kept in air tight bottles in a desiccator.

The constituents of the glasses i.e. soda and silica were chemically analysed to find out their relative proportion in the final glass (Table I).

TABLE I

Actual composition of the glasses as determined by chemical analysis

Glass No.	Mole per cent of constituents	
	SiO_2	Na_2O
1	66·01	33·98
2	75·02	24·20
3	86·51	12·80
4	95·61	4·10

Method of leaching :

1 g. powder glass of —50 +80 mesh was taken in a 100 ml. pyrex conical flask and 50 ml. of the electrolyte solution was added. The leaching was carried out in a water bath maintained at a temperature of 95-98°C for a period of 4 hours. Then, the bulk liquid phase was separated from the powder glass by filtration. The filtrate was analysed and the deplition of original cation concentration gave a measure of the ion absorbed by the corroded glasses.

Complexometric method of analysis :

Leaching was studied with cation like Ag^{+}, Ca^{+2}, Mg^{+2}, Ba^{+2} and Th^{+4} and they were all analysed with EDTA.

Ca^{+2} and Mg^{+2} were directly titrated with EDTA at pH 10·2 (Ammonia-Ammonium chloride Buffer) in presence of solochrome Black T as indicator. Ba^{+2} was determined by following the method of displacement titration i.e. on adding the Barium solution to Mg-EDTA Mg^{+2} is released in stoichiometric amount and Ba^{+2} is complexed with EDTA. The liberated Mg^{+2} was then titrated with a standard EDTA solution in the same method described above.

Th^{+4} was also determined in a direct way at pH 1-2 in presence of xylenol orange as indicator when the color change was from red to yellow. But for the estimation of Ag^{+} an indirect procedure was adopted : The aliquot silver solution was added to a solution of $K_2[Ni(CN)_4]$ (prepared by the reaction of stoichiometric quantity of $NiSO_4$ and KCN solution so that it must not contain excess Ni^{+2} or CN^{-} ions) whereby Ni^{+2} is liberated from the complex in stoichiometric amount to Ag^{+} which goes to the position of Ni^{+2}. The liberated Ni^{+2} was determined by direct titration at pH 10·2 in presence of murexide as indicator from which the amount of silver was calculated as per equation

$$K_2Ni(CN)_4 + 2\,Ag^{+} = 2\,KAg(CN)_2 + Ni^{+2}$$

TABLE II

Absorption characteristics of the different ions on the glass structure with respect to composition

Glass No.	Ion absorption in gm atoms/g. of glass with ($\times 10^4$)				
	Ag^{+}	Mg^{+2}	Ca^{+2}	Ba^{+2}	Th^{+4}
1	5·178	16·14	18·68	8·760	2·387
2	2·878	1·138	8·676	7·124	0·996
3	2·311	0·620	8·102	5·526	0·527
4	1·732	0·308	6·320	4·912	0·117

The concentrations of all the cation solutions except $Th(NO_3)_4$ were kept constant at 0·1 molar and that of Th^{+4} at 0·05 molar.

Results and Discussion

In all cases a definite portion of the cations from the aqueous phase was found to be adsorbed on the glass surface. This adsorption followed a direct relationship with the alkali content of the glasses indicating that with the hydrolytic decomposition more and more alkali ions are dissociated from the glass leaving an active silica rich negative surface which actually absorbs the cations from the solution. The rigidity of the silica network decreases with the increase in alkali content as the network is broken at several points and correspondingly some bridging links are dislodged. These spots enhance the migration of the diffusible cations from and into the glass structure. A portion of the ions also takes position of the liberated alkali ions within the network. The chemical reactivity of the corroded surface is on the other hand related to the ionic potential of the invading cations. For all the glass compositions except glass No. 1 the overall order of absorption of cations was the same as

$$Ca^{+2} > Ba^{+2} > Ag^{+2} > Mg^{+2}$$

and this may be explained on the basis of the general lyotropic series as well as the exchange potential of the cations.

When the Na_2O content increased above 24 mole percent the dissociation increased to a great extent and the abnormally high absorption of Mg^{+2} and Ag^{+} was due to their interaction with the liberated alkali ion and corresponding precipitation of the hydroxides along with the absorption on the siliceous layer.

Thus, the decomposition of glass is nothing but a preferential extraction of alkali. The thickness of the alkali deficient siliceous layer depends on the composition of glasses and the condition to which it has been subjected. Ion absorption is related to the thickness of this layer. Cations are absorbed preferentially at the boundary between the leached layer and the solution thereby setting up a dynamic equilibrium of ion exchange and the amount of this ion absorption is determined by the solvation energeies of the ions in the solution at equal concentration.

Summary

Soda-silica glasses were prepared from pure raw materials at different molar ratio of $Na_2O:SiO_2$, starting from a very weak to a most durable composition. Leaching was carried out taking the powder glasses of definite sizes with electrolyte solution of different valent cations for a definite length of time Ion adsorption on the leached alkali deficient surface was studied with respect to the glass composition from the change in the composition of the bulk liquid phase. Complexometric method of analysis with disodium salt of EDTA was adopted for this determination.

References

1. G. W. Morey, "The properties of Glass" Reinhold publishing Co., New York, 3rd printing, 103 (1947).
2. F. R. Von Hechowsky, J. Am. Cer Soc., 3, 209 (1920).
3. [illegible] and E. H. Hamilton, Jr. Res. Nat. Bur. Stand., 27, 143-157 (1941).
4. R. W. Douglas and I. O. Isard, J. Soc. Glass Technol., 33, 289T (1949).
5. A. K. Lyle, J. Am. Ceram. Soc., 26, 202 (1943).
6. R. W. Douglas and I. M. M. El-Shamy, J. Am. Ceram. Soc., 50, 1 (1967).

J. Inst. Chemists (India), Vol. XL, September, 1968

STUDIES ON COMMERCIAL GLASS. PART III

By

H. N. Das Gupta and N. K. Mitra

Department of Applied Chemistry, Calcutta University, Calcutta

(Received for publication on 7-3-68).

Since long, revelation of the nature and constitutional role of iron on colour formation and on conferment of technical or other characteristics on ferruginous glasses has been stimulating intensive research efforts. The incentive for such efforts is attributable to the conviction that familiarity with the correlation of the constitution and properties of glass can lead to the position to contrive and develop ferruginous glasses with additional scope for technical applications. Further, such an understanding renders many diverse properties of ferruginous glasses more understandable as it helps approach their elucidation from structural characteristics. A review of the useful results of the early workers in the field has been made available by Weyl.[1] It appears that the earlier ideas about the colour—forming mechanism were almost radically different from those of the modern ones. However, the contention of a few previous workers on the mechanism of the colour formation cannot, perhaps, be ruled out completely.[2] As the problem is of a complicated nature; further studies are necessary to elucidate it.

From studies involving spectrophotometric analysis[3], magnetic property measurements[4], X-ray analysis[5], electron-microscopic photograph[6] and bond-strength concept relating to iron and the surrounding oxygens[7], the modern workers have made significant advances for a better understanding of the constitutional role of iron. On some fundamental aspects, however, these investigators are divided themselves into various schools of thought. General unanimity of views is amply discernible in the concepts involving the existence of iron in the glassy matrix in multi-component states and simultaneous occurrences of iron in both electro-valent and co-valent forms, recognition of the positions like (a) interstitial holes (b) site for colloidally dispersed components and (c) dwelling spaces for iron playing the role of a net work modifier. In the concepts relating to the dependence of technical characteristics, including development of a particular hue, on the chemical nature of the chromophores and their oriented structural positions, there appears to be marked departure. In this respect, Weyl[8], Stevels[9] and Jong[10] hold views radically different from those of Moore and co-workers[3,4]. This lack in unanimity is attributable to wide differences in approach, comparison of data on uncomparable samples, and erroneous presumption about the existence of all iron in a single state of oxidation. Under condi-

tions, considered favourable for preparing highly ferrous glasses, only 90% of the total oxides could be transformed into FeO.[11]

From facts brought to light, the following deductions appear rational: a ferruginous commercial glass is very likely to be populated simultaneously by the various oxides of iron and their balance will eventually depend on the composition of the basic glass, its conditions for founding, thermal history, the percentage of the incorporated iron and its state of oxidation. Naturally, the oxides will be used preferentially in different positions. Secondly, in a glass though rich in a single form of oxide, it is not feasible to suppress the influence of the minor constituents completely. Further, even if the possibility of producing a "fully-ferric" or "fully ferrous" glass can be realised practically, no means are known for effecting concentration of the entire quantity to a particular position. The tendency of migrations towards stable locations and configurations cannot perhaps be stopped under conditions of glass formation. Again, the influence of the same chromophore from its interstitial position cannot be expected to be identical when the same assumes any one of the remaining positions. Besides, magnetic measurements are not expected to give any information about the position of the ferrous or ferric ions in glass[12]. There is also no direct evidence which has established that the same structural position is under the occupation of more than one oxide. These probable eventualities do preclude the possibility of no interference being made by the oxides constituting the minority population or by the same form of chromophore but occupying different structural positions. The inference that the colour and characteristics of a ferruginous glass are modified and influenced by the chromophores, proportionately to the concentration and location in the structure, will not be quite wrong.

A glass, containing only one form of the oxide and housed preferably in one position in the structure, will surely constitute the ideal sample for a study of the constitutional role of iron. No technique is known which may help produce such an ideal sample. It was, therefore, envisaged that evolution of means for dislodging the chromophores successively from their different positions, without affecting the glassy structure, might lead to the production of authentic samples for measurements of magnetic and or other characteristics of greater significance from the stand point of positions, if any. The inherent drawback of the latter programme relates to simultaneous removal of all the oxides from the same position and, as such, the specific role of individual oxides from a particular position can not be made known properly.

In conformity with the above programme, it was shown in a previous communication how the oxides, assumed to be present in the colloidally dispersed phase only, could be separated by bisulphate fusion and estimated.[13] The main limitation of the said process lies in the fact that the chemical nature of the dispersed oxides cannot be ascertained quantitatively. The leaching techniques which form the theme of the present communication have been found to be advantageous for partial identification of the colloidally dispersed oxides. The finely agated glass powder tends to loose quantitatively the dispersed oxides, if the same be treated with hydrochloric acid of suitable

strength and containing a few drops of nitric acid. The acid extract can be made suitable for titration with N/500 mercurous nitrate solution following the precautions advocated by the present authors in an earlier communication.[14] This gives the percentage of the total dispersed oxides as Fe_2O_3 and the experimental results are quite in agreement with those obtained by the fusion technique. If, however, this dissolution is effected in iodine monochloride solution of suitable strength and containing sufficient excess of hydrochoric acid as recommended by Hey,[15] the entire quantity of the colloidally dispersed iron also comes into solution. In this process, the ferrous component of the dispersed phase, however, liberates an equivalent quantity of iodine as fast as it passes into solution. By titrating the liberated iodine with standard potassium iodate solution according to the modifications suggested by the authors,[16] a correct measure of the ferrous iron in the dispersed phase only is obtained. This treatment with ICl does not appear to affect the ferrous iron, if any, *in other positions*. The ICl solution has been proved by Hey to be quite stable in air, both before and after the titration, and there is no danger of oxidation of the iron during dissolution. The reactions as proposed by Hey are as follows—

$$2ICl + 2Fe^{2+} \longrightarrow I_2 + 2Cl' + 2Fe^{3+}$$
$$2I_2 + IO'_3 + 6H^+ + 5Cl' \longrightarrow 5Icl + 3H_2O$$

The net over-all reaction being :

$$4Fe^{2+} + KIO_3 + 6HCl \longrightarrow KCl + ICl + 4Cl' + 4Fe^{3+} + 3H_2O$$

The direction outlined by Hey for the preparation of ICl solution is vary ikely to offer some difficulty and, as such, the modification outlined in this communication is going to prove advantageous. Further, for standardisation of the potassium iodate solution and to prevent the hydrolysis of iodine monochloride, which is formed during the titration with the iodate, the precautions as emphasized by Vogel[17] must be taken. At the end of the titration, at least 50% HCl by volume must be present.

Experimental

It should be emphasised at the outset that the modifiers and colouring components in glass are not homogeneously distributed and this fact has been established by numerous measurements and by electron-microscopic photographs (*loc. cit.*). For reproducible analytical results, the sample should, therefore, be prepared according to the procedure in vogue for those of non-uniform samples and kept separately as a stock sample. In the present case, all experiments were performed with a sample of bottle glass, the entire quantity of which was powdered and agated to 300 mesh and then electromagnetically freed from incorporated iron. The composition of the glass and its sp. gr. have been presented in Table I. The latter was determined using benzene as the immersion liquid.

TABLE I

Analysis of glass sample

Constituents (in %)		Sp. gr. of glass powder Untreated	Leached
SiO_2	67·50		
Al_2O_3	8·83	2·52	2·48
Fe_2O_3	1·85		
CaO	8·36		
MnO	Trace		
MgO	1·00		
Alkali	12·50		

Leaching with acid :

All chemicals were of A.R. quality.

A definite weight of the powder (5-6g) was treated with N/2 hydrochloric acid (50 ml) and allowed to stand for an hour. The mixture was then heated on a water-bath for 2 hrs., a few drops of conc. nitric acid added and again heated on a hot plate to reduce the volume. The solution was diluted, heated nearly to the boiling point and filtered. The residual powder was digested twice in an analogous way with the acid mixture and filtered washed free of acid and the filtrate was made to 250 ml. A definite volume of the solution was titrated with N/500 mercurous nitrate solution with the usual precautions[14]. Table II shows the results of several

TABLE II

Percentage of colloidally dispersed iron as Fe_2O

HCl leaching Found	Mean value	Bisulphate fusion Found	Mean value
0·2235		0·2221	
0·2259	0·2259	0·2251	0·2254
0·2276		0·2267	
0·2268		0·2279	

determinations by the present method. For comparison, the values obtained by the fusion technique[5] have also been incorporated.

It will be evident that the analytical values are quite comparable. In order to be sure of the complete removal of the dispersed iron by the leaching technique, the leached powder was treated with fused $KHSO_4$ and the solidified residue was tested for additional iron in the usual way when no trace of iron could be detected. The residue also did not evolve any iodine on being treated

with iodine monochloride solution. All these tests confirm the expectation of complete dissolution of the dispersed chromophores. Further, a separate sample was dissolved in HCl in CO_2 atmosphere and the leached solution gave definite indication of the presence of free Fe_2O_3 in sufficient amount.

Preparation of iodine monochloride solution :

Potassium iodide (10g) and dried potassium iodate (6·44 g.) are dissolved in water (70 ml.). Ordinarily, the iodate does not go readily into solution and, as such, the mixture is heated for effecting solution. The solution is cooled rapidly and previously cooled conc. hydrochloric acid (75 ml) is added. This pre-cooling of the acid prevents loss of iodine which gets separated from the mixture. Vigorous shaking to ensure complete solution is necessary.

When every particle goes into solution, CCl_4 or $CHCl_3$ (5 ml) is added and the mixture is shaken again. The solvent layer should indicate a faint pink colour due to slight trace of iodine. If not, a little potassium iodide solution should be adde. If, however, the organic solvent shows more than a faint pink colour, a little potassium iodate solution should be added to convert the excess iodine into ICl.

For each 3% of FeO expected, 1 ml. of ICl solution should be added.

Estimation of ferrous iron in the dispersed phase :

A.R. quality reagents required are :

(a) Potassium iodate solution, N/100
(b) Potassium iodide solution, N/100
(c) Cooled conc. HCl. (Conc. HCl is needed to prevent the hydrolysis of ICl which is produced after titration with potassium iodate soln.
(d) Iodine monochloride solution.
(e) Carbon tetra-chloride or chloroform.
(f) Pure iron.

1 ml. of 0·01N KIO_3 sol. $\equiv$ ·0007185 g. FeO

Procedure : The leaching technique was different as the ICl soln. helped accelerate iron dissolution.

The glass powder (0·5 to 1·0 g) was accurately weighed into a ground-glass stoppered 250 ml conical flask to which previously cooled 1 ml of iodine monochloride solution was added. The volume of the ICl solution should be adjusted, depending on the percentage of ferrous iron. The mixture was next treated with cooled conc. hydrochloric acid (10 ml.) and this was followed by the addition of cooled organic solvent. The addition of HCl should on no account precede that of ICl solution, as the ferrous iron is much less stable in this acid medium and suffers aerial oxidation. The flask was kept closed and shaken occasionally. The solvent layer gradually assumed the characteristic colour of iodine and thereby indicated the presence of ferrous iron. As the reaction is exothermic, external cooling of the flask was found necessary to prevent loss of the liberated iodine. Should the ferrous iron content be high, it is advisable to adopt the modified digestion method as recommended by the

authors[16] for getting accurate results. The liberated iodine was titrated with standard potassium iodate solution. Detection of the end point does not offer any special difficulty. Even then, should the end point be overshot, the mixture may be back-titrated with N/100 potassium iodide solution to the appearance of the first violet tint of the solvent. The titrated mixture should be set aside for sometime to see if the sample has been completely reacted upon by ICl solution. For incomplete reaction, the organic layer will assume violet colour of iodine again and in such a case the solution should be further titrated. In the present case no such delayed action took place. Table III shows the per-

TABLE III

Distribution of the oxides in the colloidal phase

Sl. No.	Percent FeO Found	Mean	Percent of total iron (as Fe_2O_3) A	Percent of Fe_2O_3 calculated from FeO(B)	Fe_2O_3 Rqd. to form Fe_3O_4	Difference (A-B)
1.	0·1641					
2.	0·1646	0·1645	0·2259	0·1828	0·3656	0·0431
3.	0·1650					
4.	0·1643					

centage of FeO as determined by the modified Hey's method. The corresponding calculated value for Fe_2O_3 and the theoretical Fe_2O_3 requirement of FeOto form Fe_3O_4 have been incorporated, together with the percentage of total dispersed iron, determined as Fe_2O_3 by mercurous nitrate solution. Liberation of iodine by a mixture of HF, HCl and ICl after treating the leached glass powder in the cold indicated the presence of ferrous iron in the interstitial position of the glass structure. This latter will form the subject of future communication.

Discussion

Cole has very pertinently described iron as being associated with the most complicated and confused evidence in its role as a colouring agent in glasses. Further, its power of exhibiting different valancy states has been considered to help add further complexity to the problem of colour formation. Against many such similar comments, the postulation of Moore and co-workers, envisaging the presence in glass of certain per cent of the total iron in colloidal dispersions and consisting of ferric- and ferro-ferric oxides, must be regarded as of great importance. They had also contended that these colloidally dispersed components are not in any way combined with any constituent of glass, nor are they linked to glass structure.

By collating the results of instrumental analyses and by advancing ancillary arguments, the distribution of the oxides in glass and the concept of the pre-

sence of the colloidal components have been established. As regards this latter aspect, perhaps it would have been more convincing if the presence of the components were established by direct experimental evidence. Again, the argument based on the premise "the application of magnetic measurement technique does not help give any information about the positions of the cromophores" has not strengthened the theory of Moore *et al.* These objections have been removed by chemical approach and a useful additional information, supporting the views of Moore *et al*, appears to have emerged. The ease with which the iron of this phase is leached out by acid, can be treated as a strong support in favour of the pigment producing role of these oxides. Their quantitative removal would have been a problem, if they were combined with or linked in any way with any constituent of the glass.

As will transpire, this chemical approach has not helped form any conclusion regarding the different stoichiometric ratios of the oxides, more particularly of the ferroso-ferric oxide. It is also not possible to know the compositions of those oxides that deviate from the stoichiometric ratios. As will be evident from Table III, the percentage of the FeO is appreciable and, expressed as Fe_2O_3, it constitutes 72·8% of the entire iron in the dispersed phase, leaving a balance of 27·2% as the concentration of the ferric oxide component. These facts are suggestive of the possible existence of ferroso-ferric oxide and/or of other oxides, due to the tendency towards attainment of ferrous-ferric equilibrium in the glass. The experimental data, however, can not be used to substantiate any one of these possibilities. Thus, all the ferrous oxide cannot be associated with ferric oxide forming magnetically similar Fe_3O_4. The concentration range of Fe_2O_3 is, infact, far short of the theoretical requirement of the entire ferrous oxide component. On the other hand, the concept that the preponderance of the ferrous component is due primarily to the attainment of the ferrous-ferric equlibrium appears equally improbable. Under the conditions of glass founding practice, the time allowed is not ordinarily favourable for the attainment of this equilibrium. Secondly, the fact that ferrous component of the dispersed phase has evinced sufficient resistance towards partial oxidation during finer grinding[18], does suggest that the presence of at least a small percentage of the Fe_3O_4 has to be conceded. In the absence of definite experimental evidences, the presence of the different oxides of iron may also be attributed to the various transitions between a single chromophore and Fe_3O_4, as was early hinted by Jackson[19]. However, the measurements of the magnetic properties and of the electrical conductivity, if any, with deferruginized glass samples are very likely to help present a very clear picture of the nature and concentration of the oxides. It is also expected that the results of such tests will reveal the differences between the grey component and the γ-Fe_2O_3 in regard to their magnetic properties and thermal instability.

References

1. W. A. Weyl, "Monograph of coloured Glasses", published by the Society of Glass Technology, (1950).
2. J. C. Hostetter and R. B. Sosman, J. Am. Chem. Soc., *38*, 807, 1188 (1916).
   J. C. Hostetter and H. S. Roberts, J. Am. Cer. Soc., *4*, 927-938 (1921).

3. H. Moore and S. N. Prasad, J. Soc., Glass Tech., *33,* 336 (1949) ;*ibid., 34,* 173, 193 (1950).
4. H. Moore and S. Kumar, *ibid., 35,* 58 (1951), H. Cole, *ibid., 35,* 25 (1951), Abou-El-Azm, *ibid., 38,* 101, 146, 197, 244, 271 (1954).
5. B. K. Banerjee, D.Sc. Thesis, (1957).
6. M. B. Volf, "Technical Glasses", *27* (1961).
7. H. Cole, J. Soc. Glass Tech., *35,* 5 (1951).
8. W. A. Weyl, *ibid., 22,* 265 (1943), J. Phys. Colloid Chem., *55,* 507 (1951).
9. J. M. Stevels, Verres Refract, *4,* 293 (1950).
10. J. DeJong, Thesis Delft, 36 (1952), J. Soc. Glass Tech., *38,* 57 (1954).
11. Starkie and Turner, J. Soc. Glass Tech., *15,* 365 (1931).
12. J. DeJong, *ibid., 38,* 57 (1954).
13. H. N. Das Gupta and P. Sen, J. Indian Chem. Soc., *39,* 11, 770-772 (1962).
14. H. N. Das Gupta and N. K. Mitra, J. Inst. Chemists (India), *39,* Part-IV, 185-189 (1967).
15. M. H. Hey, Mineralog. Mag., *26,* 116-118 (1941).
16. H. N. Das Gupta and N. K. Mitra, J. Inst. Chemists (India), *39,* Nov., 250-254 (1967).
17. A. I. Vogel, "A Text Book of Quantitative Analysis", 3rd Edn., 381 (1961).
18. W. F. Hillbrand, J. Am. Chem. Soc., *30,* 1120 (1908).
19. H. Jackson, Nature, *120,* 264-266, 301-304 (1927).

J. Inst. Chemists (India), Vol. XL, September, 1968

CONDUCTANCE OF TERNARY ELECTROLYTES IN DIOXANE WATER MIXTURES AT 35°C.

By

P. B. Das

Department of Chemistry
Ravenshaw College, Cuttack
(India)

The Onsager equation[1] for a completely dissociated electrolyte is $\Lambda = \Lambda^{\circ} - (A + B\Lambda^{\circ})\sqrt{C}$.....(1) where, Λ, Λ° are the equivalent conductances at concentrations 'C' and zero respectively and A and B are constants. It satisfactorily accounts for the change in the equivalent conductance with concentration. Correct evaluation of 'Λ°' can be made by extrapolating to zero concentration of the line obtained by plotting Λ against $\sqrt{C}$. However, the above method of extrapolation has been reported to be unreliable in cases of a number of electrolytes involving incomplete dissociation or ion association.[2] Davies has extended Onsager's equation and has tabulated the dissociation constants of a variety of salts especially of the higher valency type[3].

In case of symmetrical electrolytes, the ion pairs will have no net charge, though they should have a dipole moment. They will therefore, make no contribution to the electrical conductivity Fuoss and Kraus[4] and Shedlovsky[5] have developed graphical methods in which the values of 'K', the ion association constant, and 'Λ°' are simultaneously evaluated by a suitable extrapolation. However, with unsymmetrical electrolytes the position is more complicated, since the simplest and most probable type of ion association, that involving only two particles, will result in appearance of a new ionic species of a charge type, not previously present; this will contribute to the conductivity, though less than its constituent ions in the free state. The ion association of these unsymmetrical electrolytes has been studied by measuring the conductance of $MgCl_2$, $MgBr_2$, $Mg(ClO_4)_2$, $BaCl_2$, $BaBr_2$, $Ba(ClO_4)_2$, $SrCl_2$, $CaCl_2$, Na_2SO_4 and K_2SO_4 in dioxane water mixtures at 35°C and at different solvent compositions. The experimental procedure, preparation of solutions, and the experimental results have been published elsewhere.[6-10]

In the present paper the conclusions derived from the conductivity measurements of the above salts in 10, 20 and 30% dioxane-water mixtures will be discussed.

Discussion

Righellato and Davies[11] have pointed out that in case of unibivalent electrolytes, equilibria of the type,

$$M_2A \rightleftharpoons 2M^+ + A^{--} \quad \ldots\ldots (2)$$

$$A^{--} + M^+ \rightleftharpoons MA^- \quad \ldots\ldots (3)$$

exist. The dissociation constant 'K' for MA^- is, therefore, given by:

$$K = \frac{[M^+]\,[A^{--}]}{[MA^-]} \times \frac{f_{M^+} \times f_{A^{--}}}{f_{MA^-}} \quad \ldots\ldots (4)$$

Assuming a similar type of behaviour in the case of biunivalent electrolytes, namely, $MgCl_2$,

$$K_{MgCl^+} = \frac{[Mg^{++}]\,[Cl^-]}{[MgCl^+]} \times \frac{f_{Mg^{++}} \times f_{Cl^-}}{f_{MgCl^+}} \quad \ldots\ldots (5)$$

where 'f's represent the activity coefficients of the corresponding ions and the square bracket indicates the molar concentration.

Following the method of calculation adopted by Jenkin and Monk,[12] the first stage of dissocation is assumed to be complete, and we have only to deal with the second equilibrium:

$$MgCl^+ \rightleftharpoons Mg^{++} + Cl^-$$

Let 'm' represent the molar concentration of $MgCl^+$ and 'α' be the fraction that does not take part in ion association, then

$$\begin{aligned} MgCl^+ &= (1-\alpha)\ m\ ; \\ Mg^{++} &= \alpha m; \\ Cl^- &= m\ (1+\alpha)\ ; \end{aligned}$$

$$\text{so that } K_{MgCl^+} = \frac{\alpha\,(1+\alpha)\ m}{(1-\alpha)} \times \frac{f_{Mg^{++}} \times f_{Cl^-}}{f_{MgCl^+}} \quad \ldots\ldots (6)$$

The solution as a whole can be regarded as containing two types of salts; (i) biunivalent $MgCl_2$ yielding Mg^{++} and Cl^-, and (ii) uniunivalent $MgCl^+$ and Cl^-. For the 2—1 electrolyte, the equivalent conductance in given by the expression:

$$\Lambda_{2-1} = \Lambda^\circ_{2-1} - (A_{2-1} + B_{2-1}\ \Lambda^\circ_{2-1})\sqrt{I} \quad \ldots\ldots (7)$$

and for the 1-1 electrolyte:

$$\Lambda_{1-1} = \Lambda^\circ_{1-1} - (A_{1-1} + B_{1-1}\ \Lambda^\circ_{1-1})\sqrt{I} \quad \ldots\ldots (8)$$

where A and B are Onsager's constants, Λ° is the equivalent conductance at zero concentration, and Λ that at the actual ionic strength, I.

$$I = \tfrac{1}{2}\{[Cl^-] + [MgCl^+] + 4[Mg^{++}]\} = m\,(1+2\alpha) \quad \ldots\ldots (9)$$

R_{2-1} and R_{1-1} the specific conductances of the 2-1 and 1-1 types of salts respectively, are given by:

$$R_{2-1} = \frac{2cm \times \Lambda_{2-1}}{10^3} \text{ and}$$

R, the specifice conductance of the electrolyte containing a mixture of the two types, may be therefore, expressed as:

$$R = R_{2-1} + R_{1-1} = \{2\alpha m \Lambda_{2-1} + (1-\alpha) m \Lambda^{1-1}\} 10^{-3}$$

or, $$\frac{10^3 R}{2m} = \alpha \Lambda_{2-1} + \tfrac{1}{2}(1-\alpha) \Lambda_{1-1} \quad \ldots\ldots\ldots(10)$$

where 'Λ' is the measured equivalent conductance.

The Onsager constants A and B for 2-1 and 1-1 types are calculated theoretically. Λ° 2-1 has been determined from the extrapolation of the plot of Λ against $\sqrt{C}$. The value of Λ° 1-1 has been calculated by taking the mobility of $MgCl^+$ as two third of the bivalent Mg^{++} (Righellate *et al.*[11]) and by making use of the mobility of the Cl^-, determined by Patnaik *et al*[13]. The two unknown quantities are 'α' and 'I'. For the determination of 'α', the method of approximation used is as follows. Let 'α' be equal to unity, when an approximate value of I is calculated, according to equation (9). This value of I is used for calculating a truer value of α and this process is repeated till a constant value of α is obtained. By using this constant value of α and the activity coefficient calculated from the usual Debye—Hückel expression, the dissociation constants at vorious concentrations have been determined according to equation (5). The same procedure was followed for the ion pairs $MgBr^+$, $Mg(ClO_4^+)$, $BaCl^+$, $BaBr^+$, $Ba(ClO_4^+)$ $SrCl^+$, $CaCl^+$, $NaSO_4^-$ and KSO_4^-. In case of Na_2SO_4, the plot of Λ against $\sqrt{C}$ is not linear, so Λ° has been obtained from the extrapolation of the plot of $\Lambda + b\sqrt{C}$ against 'C' (Bevan and Monk[11]), where 'b' is the calculated coefficient of Onsager's conductivity expression. The Λ° and pK values for the salts and ion pairs respectively have been tabulated in Table I and Table II.

Several attempts have been made to estimate the individual ionic conductivities from those of salts on a hydrodynamic basis. Walden[15] found that the

TABLE I

Electrolytes	Equivalent conductance of zero concentration (Λ°)		
	10% Dioxane	20% Dioxane	30% Dioxane
$MgCl_2$	146·4	135·8	113·6
$MgBr_2$	124·0	112·0	97·5
$Mg(ClO_4)_2$	164·0	124·0	105·0
$BaCl_2$	148·4	140·4	116·2
$BaBr_2$	165·5	150·0	126·3
$Ba(ClO_4)_2$	165·5	128·5	108·0
$SrCl_2$	140·0	133·5	116·0
$CaCl_2$	145·0	128·0	118·0
Na_2SO_4	174·5	150·5	118·0
K_2SO_4	163·5	136·0	107·5

TABLE II

Ion pairs	pK values of the ion pairs 10% Dioxane	20% Dioxane	30% Dioxane
MgCl+	—	1·305	0·686
MgBr+	—	0·285	0·931
$Mg(ClO_4)$+	0·842	1·266	1·600
BaCl+	0·985	1·243	1·564
BaBr+	0·637	0·968	1·086
$Ba(ClO_4)$+	1·686	1·391	1·836
SrCl+	1·060	1·570	1·710
CaCl+	1·390	1·619	2·051
$NaSO_4$−	1·265	1·574	1·708
KSO_4−	0·002	1·025	1·266

limiting equivalent conductivity of tetraethylammonium picrate in a wide variety of solvents including water conformed closely with the formula :

$$\wedge^{\circ}\eta_0 = \text{constant.}$$

which is derivable from Stokes' law and is known as Walden's rule. A similar constancy was found for tetramethylammonium picrate. The product, $\wedge^{\circ}\eta_0$ is practically independent of temperature[16], but most pronounced variations with temperature are found in systems containing hydrogen ions or highly associated or viscous solvents. Very large spherical ions would be nearly free from solvation because of the low charge density on their surfaces and the magnitude of their radii would be independent of the nature of the solvent. Such ions would be the ideal condition of spheres moving through homogenous media, as required by Stokes' law. Ions of small size or of unsymmetrical shape, would be expected to show serious departures from Walden's rule.

This departure has been found by Griffith and Lawrence,[17] Griffith, Lawrence and Pearce[18] etc. It indicates that solvation change is occurring. It can be seen from Table III that the product $\wedge^{\circ}\eta_0$ is not a constant. This shows that Walden's product has not been too successful. The simple modification of the Walden product relating the conductances and the dielectric constants of the solvents $\wedge^{\circ}\eta_0/D$, according to van Rysselberghe and Fristrom[19] is also not constant and hence it does not seem to apply (Table IV) to the solution of all the salts in dioxane-water mixtures. The condition under which the preceding are obeyed, i.e. large ions with low surface charge density and minimum solvation effects, are apparently not fulfilled in these solutions. The recent calculation by Fuoss[20] on the dependence of Walden product on the dielectric constant showed that the calculated size of the ionic species depends on the nature of the solvents. So the deviation of Walden product from constancy is understood as being due to an increase in viscosoty attributed to the electrostatic coupling between the moving ions and the solvent dipoles. The same conclusion was also drawn from the 'B' values of the same salts, obtained from viscosity measurements[21].

TABLE III

Electrolytes	$\Lambda^{o}\eta_{o}$		
	10% Dioxane	20% Dioxane	30% Dioxane
$MgCl_2$	1·264	1·414	1·337
$MgBr_2$	1·069	1·166	1·147
$Mg(ClO_4)_2$	1·414	1·229	1·234
$BaCl_2$	1·276	1·499	1·367
$BaBr_2$	1·427	1·562	1·486
$Ba(ClO_4)_2$	1·427	1·110	1·270
$SrCl_2$	1·207	1·359	1·364
$CaCl_2$	1·250	1·308	1·388
Na_2SO_4	1·504	1·566	1·385
K_2SO_4	1·406	1·416	1·264

TABLE IV

Electrolytes	$\Lambda^{o}\eta_{o}/D$		
	10% Dioxane	20% Dioxane	30% Dioxane
$MgCl_2$	0·0191	0·0245	0·0272
$MgBr_2$	0·0161	0·0202	0·0233
$Mg(ClO_4)_2$	0·0213	0·0213	0·0251
$BaCl_2$	0·0192	0·0259	0·0279
$BaBr_2$	0·0215	0·0270	0·0302
$Ba(ClO_4)_2$	0·0215	0·0192	0·0258
$SrCl_2$	0·0182	0·0235	0·0277
$CaCl_2$	0·0188	0·0227	0·0288
Na_2SO_4	0·0226	0·0271	0·0282
K_2SO_4	0·0212	0·0245	0·0257

On the assumption that purely coulombic forces exist between the constituent ions, Bjerrum[22] has shown that the distance 'a' between the centre of the two ions at their closest distance of approach can be calculated from the knowledge of the reciprocal equilibrium constant K^{-1} of the ion. The equation is, $K^{-1} = \frac{4\pi N}{1000}\left(\frac{|z_1 z_2|\varepsilon^2}{DRT}\right)^3 Q(b)$ .....(11)

where the symbols have their usual meanings and

$$Q(b) = \int_{z}^{v} e^{x} b^{-4} dx.$$

where $x = \frac{|z_1 z_2|\varepsilon^2}{DrRT}$ and $b = \frac{|z_1 z_2|\varepsilon^2}{DaRT}$.

The values of Q(b) as defined has been tabulated[23] for different values of 'b' from 1 to 80 and hence 'a' can be calculated. On the other hand, if the ions constituting the electrolyte are regarded as obeying Stoke's law, then the radius 'r' of an ion can be found from the known values of the limiting mobi-

TABLE V

Ion Pairs	Diameter of the ion pair (aA°)					
	10% Dioxane		20% Dioxane		30% Dioxane	
	Bjerrum's equation	Stoke's Law	Bjerrum's equation	Stoke's Law	Bjerrum's equation	Stoke's Law
MgCl+ ...	—	—	1·13	1·60	1·06	1·74
MgBr+ ...	—	—	0·87	4·33	1·00	4·72
$Mf(ClO_4)$+ ...	0·60	3·85	0·55	3·82	0·81	3·78
BaCl+ ...	1·12	4·45	1·20	3·39	1·23	3·43
BaBr+ ...	1·43	5·11	1·50	4·21	1·69	3·96
$Ba(ClO_4)$+ ...	0·55	4·17	0·48	3·71	0·40	3·64
SrCl+ ...	0·54	3·27	0·42	2·42	0·59	2·43
CaCl+ ...	0·31	2·74	0·15	2·53	0·23	2·37
$NaSO_4$− ...	0·39	3·44	0·51	3·26	0·65	3·59
KSO_4− ...	1·13	1·44	1·38	1·59	1·76	2·00

lity for the ion. The diameter of the ion pair is calculated by adding the cationic and anionic radii. The ionic diameter calculated by both the methods are recorded in table V. From the data in table V, it can be said that although the size of the ion pairs is of the right order, they are not in good agreement. Bjerrum's 'a' is smaller than the stoke's radii (for all the salts), which indicates that there is greater interaction between the ions than would be expected if only electrostaic forces are involved.x It is seen from the results that an appreciable change of Bjerrum's 'a' occurs in solution (in cases of all salts) possibly because of solvation. Hence, it can be stated that when the dioxane and the water content of the solvent are changed, the ions orient the available water and dioxane molecules in different proportions. The solvation sphere thus changes according to the nature of the electrolyte.

It is usually accepted[24] that the dissociation of an electrolyte is dependent on two factors, namely, the dielectric constant and the parameter 'a' and many attempts have been made to study the variables separately[25, 26]. As far as 'D' is concerned, it is usual to assume that no changes in the solvation occur, i.e., ionic size and the bulk 'D' controls the association and dissociation processes[25, 26, 27]. This is generally shown by the linearity of the plot of pK against 1/D. But in the present case the plot of pK against 1/D is not linear i.e. 'a' is not constant (Graph is omitted). This discrepancy indicates that both the decrease in the dielectric constant and the change in the Bjerrum's parameter 'a' are responsible for the decrease in 'K'.

ACKNOWLEDGEMENT

The author is thankful to Dr. D. Patnaik, Professor of Chemistry for encouragement during the work.

REFERENCES

1. Onsagar, Physikal, *Z*, *28*, 277 (1927).
2. Harned and Owen, "The Physical Chemistry of Electrolytic Solution."
3. J. C. S. Dalton, *140*, 2093 (1958).

4. Fuoss and Kraus, J. Am. Chem. Soc., *55,* 739 (1933).
5. Shedlevsky, J. Fronkin. Inst., *225,* 739 (1938).
6. P. B. Das, P. K. Das and D. Patnaik, J. Ind. Chem. Soc., *36,* 410 (1959).
7. P. B. Das, Ind. J. App. Chem., *26,* 81 (1963).
8. P. B. Das and D. Patnaik, ibid., *38,* 411 (1961).
9. S. Devi and P. B. Das, ibid., *42,* 500 (1965).
10. P. B. Das, Jour. Inst. Chemists (Communicated).
11. Righellate and Davies, Trans. Far. Soc., *26,* 592 (1930).
12. Jenkin and Monk, J. Chem. Soc., 68 (1951).
13. D. Patnaik *et al.,* J. Ind. Chem. Soc., *34,* 56 (1957).
14. Bevan and Monk, J. Chem. Soc., 1392 (1956).
15. Walden and Busch, Z. Phys. Chem., *113,* 429 (1926), and Walden and Birr. ibid., *153A,* 1 (1931).
16. Ulich, Fortschritte, Chem., *18,* 10 (1926).
17. Griffith and Lawrancen, J. Chem. Soc., 1208 (1955).
18. Griffith, Lawrence and Pearce, ibid., 3998 (1958).
19. Van Rysselberghe and Fristrom, J. Am. Chem. Soc., *67,* 680 (1945).
20. Fuoss, Proc. Natt. Acad. Sci. U. S., *45,* 807 (1959).
21. P. B. Das (Unpublished).
22. Bjerrum, Eet, Kgl Danske, VII, *9,* 2 (1926).
23. Robinson and Stokes, "Electrolyte Solutions", Appendix 14, (1955).
24. Griffith and Lawrence, J. Chem. Soc., 2927 (1955).
25. James, ibid., 1094 (1950).
26. James, ibid., 153 (1951).
27. Dunsmere and Jones, ibid., 2925 (1951).

INFORMATION

This Institution is registered under the Registration of Societies Act XXI of 1860 (Regd. No. 6059/107 of 1928-1929).

FELLOWSHIP (F.I.C.)—Suitable for a chemist, not below 28 years, who in the opinion of the Council has done original research work of a high order, or has been engaged in important analytical, production, consulting or similar work of a general or specialised character. The nature and responsibility of the positions held by him will be taken into consideration along with any thesis or report on technological subjects submitted by him.

ASSOCIATESHIP (A.I.C.) *without examination*—Suitable for a chemist, not below 23 years, engaged in the *practice* of chemistry for at least five years in a manner satisfactory to the Council.

ASSOCIATESHIP (A. I. C.) *by examination*—A. I. C. diploma in Group A (Analytical Chemistry) obtained by examination is recognised by the Union Government as equivalent to M.Sc. degree in Chemistry for purposes of recruitment of chemists and is recognised in the Indian Drugs Act. Further details may be obtained from the office of the Institution.

MEMBERSHIP—Suitable for a graduate, with chemistry as one of the subjects, not below 21 years.

Application to any of these categories should be submitted in the prescribed form for that category. The Admission fee and Annual subscription for Fellowship are Rs. 20/- and Rs. 24/-, for Associateship Rs. 12/- and Rs. 16/- and for Membership Rs. 8/- and Rs. 12/- respectively. No Admission fee is payable for a change in the category of the corporate membership. Six issues of the Journal of the Institution of Chemists (India) and the four issues of the Proceedings of the Institution of Chemists (India) are available to all corporate members without extra charge.

Firms, institutes or individuals, not otherwise eligible for above membership may subscribe to the Journal of the Institution of Chemists (India), inland rate (annual)—Rs. 30/- (single issue—Rs. 6/-); foreign rate (annual)—$6·00 (U.S.A.) or 50 Shillings or Rs. 45/- (single issue—$1·00 or 9 Shillings or Rs. 8/-). The annual Subscription for the Proceedings of the Institution of Chemists (India) is Rs. 10/- (single copy Rs. 3/-).

In order to avoid misdelivery of mails all members and subscribers are particularly requested to intimate the office of the Institution about any change of address at the earliest.

All communications should be addressed to the Hony. Secretary, Institution of Chemists (India), Chemical Department, Medical College, Calcutta-12.

A RIGHT drop in the RIGHT place..

That's what makes for QUALITY. Calchemico does not leave anything to CHANCE !

Mere intention to do the right thing is not enough. One needs the wherewithal. Calchemico has got it — men, equipment and efficiency. That's why they lead in their field of activity. Success does not come to any one by chance and wishful thinking. One has to, deserve it.

CHEMICALS—Heavy, Fine & Technical.
PHARMACEUTICALS—Drugs & Galenicals, Medicinal Specialities.
LABORATORY RE-AGENTS
SOAPS & COSMETICS—viz., Margo Soap, Neem Tooth Paste. etc.
ESSENTIAL OILS & AROMATIC CHEMICALS,
DISINFECTANTS & ANTISEPTICS.

THE CALCUTTA CHEMICAL CO., LTD.

Head Office—35, PANDITIA ROAD, CALCUTTA-29

BRANCHES & DEPOTS ALL OVER INDIA

IN ALL HAEMORRHAGES—

TWO OUTSTANDING STYPTICS . . . .

STYPTOVIT

TABLET

TRIPLE ACTION STYPTIC
FOR ORAL USE

Each tablet contains :

Adrenochrome Monosemicarbazone	...	0·33 mg.
Vitamin K_3	...	10 mg.
Vitamin C	...	100 mg.
Vitamin P (Rutin)	...	50 mg.
Calcium Gluconate	...	0·33 gm.
Vitamin D (Calciferol)	...	500 I.U.

STYPTOCHROME

INJECTION

PARENTERAL HEMOSTAT
IN EMERGENCIES

Each 2 ml. contains :

Adrenochrome Monosemicarbazone	...	0·75 mg.

CORRECTS COAGULATION ⊖ STRENGTHENS CAPILLARY WALL
REGULATES VASCULAR PHENOMENON

MOST SELECTIVE ⊖ EFFECTIVE VASOCONSTRICTOR, at the point of Bleeding

NEUROPHIN

INJECTION

COMPOSITION :

Each ml. of 2 ml. ampoule contains :

Cyanocobalamin (Vitamin B_{12}) U.S.P.	...	500 mcgm.
Thiamine Hydrochloride (Vitamin B_1) B.P.	...	50 mg.
Pyridoxine Hydrochloride (Vitamin B_6) U.S.P.	...	50 mg.

For details please write to :

DOLPHIN LABORATORIES PRIVATE LTD.

1, ALLENBY ROAD • CALCUTTA-20 • Phone : 47-4229

CALCUTTA INDUSTRIAL CHEMICALS & MINERALS CO. PRIVATE LTD.

43, DHARAMTOLA STREET,

CALCUTTA - 13

PHONES: { 24-1004 / 24-1005 }

GRAMS: { "GANDHAK" Calcutta. }

Manufacturers of :

GLUE, ALUMINIUM AND ZINC STEARATES, COPPER, LEAD, AND MANGANESE NAPHTHENATES, WHITE AND BROWN FACTICE ETC.

World and Paper !

THE WORLD IS MOVING ROUND AND
PAPER RUNS ROUND THE WORLD
AND
WE DEAL IN PAPERS
THAT CONTROL WORLD PROBLEMS

Distributors:

THE TITAGHUR PAPER MILLS CO., LTD.
THE BENGAL PAPER MILL CO., LTD.

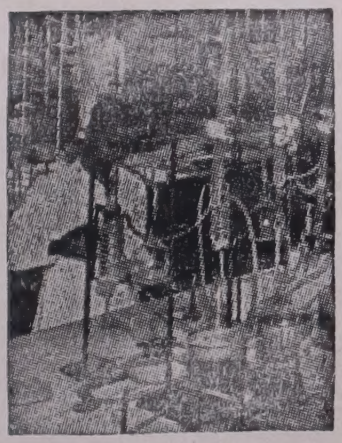
Dealers:

ALL SORTS OF LOCAL AND FOREIGN PAPERS, BOARDS, PRINTING INKS AND BOOK-BINDING MATERIALS.

PROKASH CHANDRA SINHA & SONS

65, BAITAKHANA ROAD,
CALCUTTA 9
Phone: 53-1379

For
QUALITY CONTROL
ANALYSIS AND ASSAYS



By MODERN METHODS AND EQUIPMENT UNDER EXPERT SUPERVISION

YOU MAY SAFELY DEPEND ON US

SMITH, STANISTREET & CO. LTD.,
HEAD OFFICE, FACTORY & LABORATORY,
18, CONVENT ROAD, CALCUTTA-14.

INSTRUCTION TO AUTHORS

The Journal of the Institution of Chemists (India) is suitable for publication of original papers and notes (review in special cases) on various aspects of Chemistry. A paper found unsuitable for publication is not returned.

The manuscript should be submitted in duplicate. It should be neatly typed with double line and marginal spacings in the final form for printing according to the usual get up of this Journal. No substantial alteration is allowed at the proof stage. Foot-notes should be avoided as far as possible, tables and figures minimum in number and size and should not represent the same data. Tables and figures should be numbered consecutively and drawings in black ink. References, numbered consecutively, should be at the end of the paper. In the text these should be indicated by superior numbers (above the line).

Arrangement of references should be as follows: J. G. Kane and G.M. Randive, J.Sci.Ind.Res.India, 10B,62(1951). H.W. Loesecke, Drying and Dehydration of Food, Reinhold, New York, 2nd Edn. p.93 (1943).

Contributors will receive 25 reprints free of charge. Requests for additional reprints, which will be charged for, should be made while submitting a paper.

BENGAL CHEMICAL & PHARMACEUTICAL WORKS LD.

Pioneer Indian Manufacturers of Pharmaceuticals & Chemicals.

Manufacturers of :

Pharmaceutical Chemicals :

Caffeine and its salts, Potassium Citrate B.P., I.P., Sodium Citrate B.P., I.P., Potassium Acetate B.P., I.P., Potassium Iodide B. P., I.P., Sodium Iodide B.P., I.P., Ferri et Ammon Citrate B.P., I.P. and various other Pharmaceutical Chemicals.

Heavy & Reagent Quality Fine Chemicals :

Acid Sulphuric Coml., Pure, C.P., B.P., A.R., Acid Hydrochloric Coml., Pure, C.P., B.P., A.R., Acid Nitric Coml., Pure C.P., B.P., A.R., Sodium Citrate A.R., Potassium Citrate A.R., Magnesium Sulphate A.R., Sodium Sulphate Anhydrous A.R., Potassium Iodide A.R., Sodium Chloride A.R., Zinc Sulphate A.R. Ammonium Nitrate A.R. and various other reagent quality fine chemicals for Laboratory purposes.

Please refer your enquiries for the above items and other chemicals in the line to :—

BENGAL CHEMICAL

6, GANESH CHUNDER AVENUE,
CALCUTTA - 13 • INDIA.

Printed by Shri S. N. Mitra at Sri Gouranga Press Private Ltd., 5, Chintamani Das Lane, Calcutta-9, and also published by him from the office of the Institution of Chemists (India), Chemical Department, Medical College, Calcutta-12.

TROMBAY UNIT

OF

The Fertilizer Corporation of India Limited

offer

* UREA (Technical Grade)
* AMMONIA
* SULPHURIC ACID 98%
* NITRIC ACID 60%
* METHANOL
* ARGON
* LIQUID NITROGEN

Please contact

MARKETING DIVISION

The Fertilizer Corporation of India Ltd.

TROMBAY UNIT, Bombay-74

OR

AREA OFFICES (TROMBAY UNIT) at:

5-10-173, Fateh Maidan Road,
Hyderabad (A.P.)

13, Lindsay Street,
Calcutta-16 (West Bengal)

1/2 Hayes Road,
(Behind Reserve Bank of India),
Bangalore-25.